

MATRIX ISOLATION SPECTROSCOPY:
MAGNETIC CIRCULAR AND LINEAR DICHROISM

BY

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To Donna and Alex

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MATRIX ISOLATION SPECTROSCOPY:
MAGNETIC CIRCULAR AND LINEAR DICHROISM

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Magnetic Circular Dichroism (MCD) and Magnetic Linear Dichroism (MLD) are powerful techniques which can be used to study matrix isolated atoms and molecules. These spectroscopic probes allow one to thoroughly characterize the nature of entrapped species by measuring such quantities as their ground/excited state spin-orbit coupling constants, Lande g factors, site symmetry, and Jahn-Teller couplings with the rare gas cage.

Application of the method of moments to the lower energy $2S \rightarrow 2P$ absorption and MCD transitions of matrix isolated alkali and noble metal atoms has revealed 1) a decrease in the excited spin-orbit constant in the order $Ar > Kr > Xe$, (2) spin orbit constants which are greater than the gas phase value in some cases (Ex. $Au/Ar, Kr, Xe$), (3) less than the gas phase value in other cases (Ex. $Cu/Ar, Kr$), and (4) negative in still other cases (Ex. $Li/Ar, Kr, Xe$). A supermolecule model nicely accounts for all of these observations.

The MCD saturation technique applied to Re isolated in a Kr lattice shows that Re occupies a substitutional site and possesses a large ground state crystal field splitting. The ground state, which is nominally $^6S_{5/2}$, is SO and crystal field mixed with higher lying states thus resulting in the large matrix splitting.

A general MCD/MLD saturation theory similar to that used for Re/Kr is developed to treat the case of an arbitrary atomic ground state ($^{2S+1}L_J$) trapped in a matrix site of any symmetry. This is applied to the case of Ni which is known to possess a $^3D_3$ ground state in Ar, Kr, and Xe matrices.

Orientationally averaged MCD and MLD Faraday parameters are derived for matrix isolated randomly oriented linear molecules. These should prove useful in assigning observed electronic transitions of rare gas entrapped linear molecules.

In the course of our MCD/MLD work, a heretofore unknown Lande g factor sum rule was discovered. Experimental g factors were found to obey this rule with increasing deviation as one proceeds from the first to third transition series. Finally, expressions are derived for computing the number of isotopomers of a given cluster. Isotopically mixed clusters are an important means of identifying the size and geometry of matrix isolated clusters.

CHAPTER 1 INTRODUCTION

Matrix isolation is a technique whereby reactive atoms molecules, and ions may be trapped in an inert matrix at cryogenic temperatures. Developed in 1954, this method typically isolates the species to be studied in a large excess of rare gas. By rigidly isolating reactive species in such a cage, one can study their behavior at leisure. The low temperature and rigid host insure that the guest is normally present in its ground electronic and vibrational states. Due to the inert nature of the rare gases, perturbation of the guest species by the matrix is usually considered to be small. In fact, infrared frequency shifts of matrix entrapped species are typically 1-2 percent of their gas phase values. Hence the behavior of the trapped atom or molecule usually parallels that of the isolated gas phase species. In certain cases however, matrix effects can be substantial, and these are discussed below.

The methods used to investigate matrix isolated species are usually spectroscopic in nature and include electronic absorption and emission, IR, Raman, and ESR. In addition, the powerful techniques of magnetic circular dichroism (MCD) and magnetic linear dichroism (MLD) are ideally suited to the

study of matrix isolated species as we now demonstrate. Whereas MCD corresponds to the differential absorption of left and right circularly polarized light propagating in the direction of an applied magnetic field, the complementary technique, MLD, corresponds to the differential absorption of light polarized parallel and perpendicular to the applied field. Using these spectroscopic probes, it is possible to study the following features of matrix isolated species:

1. spin-orbit coupling
2. crystal field splittings
3. spectral assignments
4. g factors
5. vibronic (Jahn-Teller) perturbations

In subsequent chapters, these various aspects of MCD and MLD are explored.

In chapter 2, trends in the ^2P excited state spin-orbit (SO) constants for various matrix isolated metals are analyzed. A supermolecule model is developed in which the metal atom is perturbed by a tetradecahedral array of rare gas atoms. Using a basis set of p orbitals on each atom, the matrix perturbed metal atomic orbitals are constructed and subsequently used to construct the SO matrix. Diagonalization results in a SO reduction factor, k, which depends upon the rare gas mixing coefficients, overlap integrals, and the free atom SO constants for both the metal and rare gas atoms. The resulting master equation for k qualitatively accounts for the

3 major classes of k values experimentally observed. In addition, numerical evaluation of the reduction factor produces results which are in reasonable accord with experiment.

In chapter 3, the crystal field splitting of the nominal ^6S ground state of Re matrix isolated in Kr is investigated using MCD saturation theory. Since the ^6S state is spherically symmetric, it is necessary to mix in higher electronic states to account for such a crystal field effect. Using both the crystal field (O_h) and SO Hamiltonians, one can mix the ^4P and ^4G excited states into ^6S . The resulting eigenstates are used to evaluate the required ground state eigenvalues and transition moments. It is then a simple matter to derive a theoretical expression for the MCD as a function of both the temperature and crystal field parameter. By fitting the temperature dependent MCD data to the theoretical equation, a crystal field splitting of 7.5 cm^{-1} is found. This is large enough to preclude the observation of any low temperature X-band ESR spectrum.

Chapter 4 represents a generalization of the approach used in chapter 3 to the case of any atom matrix isolated in a crystal field of arbitrary symmetry. Unfortunately, since the off diagonal Zeeman matrix elements (crystal field basis) had to be neglected, the general MCD and MLD saturation equations derived will not be very useful except for the case of very small magnetic fields. It appears that an accurate

analysis of saturation data requires a complete diagonalization of the full Zeeman-crystal field matrix.

In chapter 5, we look at yet another manifestation of the utility of MCD and MLD. The assignment of atomic spectral transitions (angular momentum changes) is easily made from the signs of the observed MCD and MLD bands. The Faraday parameters, C_0 (MCD) and G_0 (MLD), are the important theoretical quantities that govern the observed band signs for low temperature paramagnetic atoms. In this chapter, the atomic formalism is extended to the case of linear molecules randomly oriented in a rare gas matrix. The linear molecule Faraday parameter expressions associated with degenerate ground and/or excited states are developed. From these results, it is seen that the spectral band signs can be used to unambiguously assign linear molecule transitions in analogy to the atomic case.

During the course of our MCD work on matrix isolated Re, an apparently unknown g sum rule was serendipitously discovered. It is shown in chapter 6 that the average g factor associated with a particular Russell-Saunders term is exactly equal to the free spin value, g_s ($S > L$), or the pure orbital value, g_l ($L > S$). Comparison of this prediction with experimental values for various spectroscopic terms of V, Mo, and Re is then made. The agreement is good with increasing deviation observed as one proceeds to the heavier elements; this is due to the well known departure from Russell-Saunders

coupling associated with elements of high atomic number. Extension of this g sum rule to the case of nuclear hyperfine coupling is then made resulting in a similarly simple result.

In chapter 7, we digress from our work on MCD and MLD, and instead consider another aspect of matrix isolation spectroscopy. Whereas MCD and MLD tend to probe the electronic nature of atoms and molecules, infrared (IR) spectroscopy is more suited to the study of molecular structure; the utility of isotopically labelled molecules in this context is well known. Simple formulae are derived for computing the total number of isotopomers of a monoelemental linear molecule. Subsequently, a more general treatment, based upon the Polya enumeration method, is developed for the general symmetry case. The resulting equations should prove useful in elucidating both the size and shape of a matrix isolated cluster based on the number of IR bands observed in the spectrum of the isotopically labelled molecule.

CHAPTER 2
THE EXTERNAL HEAVY ATOM EFFECT: THEORY OF SPIN-ORBIT
COUPLING OF ALKALI AND NOBLE METAL ATOMS IN RARE GAS MATRICES

Introduction

The heavy atom effect is the perturbation of the spin-orbit coupling in an atom or molecule due to a nearby atom of high atomic number. The internal heavy atom effect,¹⁻² first studied by McClure,³ involves a heavy atom perturber chemically bound to the species under study. If the heavy atom perturber is not bound but resides in the solvent environment, a phenomenon initially investigated by Kasha,⁴ it is referred to as the external heavy atom effect.¹⁻² Since these pioneering works, a large number of studies, both theoretical⁵⁻¹¹ and experimental,^{1,2,12-20} have been performed, particularly on aromatic hydrocarbons. It is now well known^{1,2} that in aromatics the heavy atom effect greatly influences such processes as singlet-triplet absorption probabilities, excited singlet to triplet intersystem crossing rates, and phosphorescence lifetimes. The mechanism governing the perturbation by the heavy atom, while not precisely known, is generally acknowledged to involve the spin-orbit enhanced admixture of singlet and triplet states.

These processes reflect only indirectly the influence of the heavy atom perturber. The direct measurement of the heavy atom effect, i.e. the spin-orbit splitting in an aromatic molecule, is a more difficult task due to the inherent smallness of the effect in first row atoms, as well as to the simultaneous presence of spin-spin splittings of similar magnitude.

Direct spin-orbit splittings have been observed²¹⁻²⁴ for F centers in alkali halide lattices (e.g. KI, KCl, RbBr) and, although not couched in the terminology of the heavy atom effect, are generally seen to increase with the atomic number of the cation and anion of the host lattice. Elegant theoretical developments have been reported²⁵⁻²⁸ to explain these observations, the most successful of which employs a vacancy centered wavefunction which is orthogonalized to the crystal ion functions

Recently, experimental results from magnetic circular dichroism (MCD) and U.V./Visible absorption studies²⁹⁻³⁴ of the noble and alkali metal atoms in rare gas matrices (Ar, Kr, and Xe) have been analyzed using a band moment analysis method, originally applied by Henry, Schnatterly, and Slichter²⁵ to the study of F centers. This analysis permits the extraction of the excited ^2P state spin-orbit splitting and its dependence on rare gas matrix atom type, and thus affords a direct measure of the external heavy atom effect. Sufficient data have now been reported to show that there is

a profound influence by the rare gas atoms on the metal's spin-orbit splitting. Certain trends have begun to emerge. 1) The spin-orbit (SO) reduction factor, k , decreases for all metals as the rare gas atomic number increases. 2) For Au, k greater than one are observed³⁴ in all of the rare gases. 3) Positive k are observed for Cu in Ar and Kr while a negative k is found for Cu/Xe²⁹, and 4) negative k are found for Li in all of the rare gases,^{31,32} K in Kr and Xe^{32,33} and Na in Xe.³² There are still significant gaps in the experimental data available. Nevertheless the observations to date point to a complex phenomenon which depends not only on the properties of the rare gas and metal atom, but also on properties due to their interaction.

Our goal is to explain on a unified theoretical basis the trends in the observations set forth above. We do this by introducing a supermolecule model and calculating the SO splitting directly. Our approach has features which differ from older, previous studies. In the next section a short background of the spectroscopic observations, analysis methods and results for the noble and alkali metals in matrices is given. This is followed by the theoretical approach used here. After discussing certain aspects of the theory and some of its limitations, conclusions are drawn.

Background

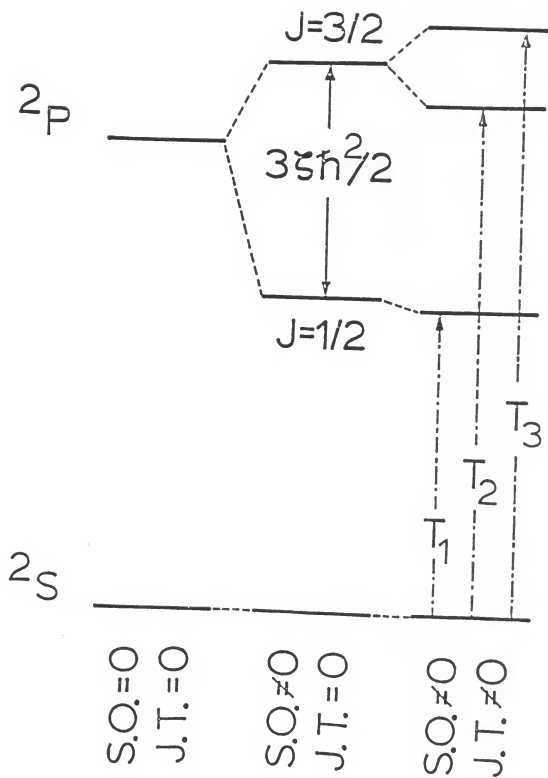
The particular electronic transition studied here is the $^2P \leftarrow ^2S$ (electronic configuration ... $np^1 \leftarrow \dots ns^1$). SO coupling in the gas phase atom splits the ^2P state into 1/2 and 3/2 multiplets; the separation between these free atom states is $3\zeta\hbar^2/8\pi^2$, where ζ is the SO coupling constant. Although a doublet is expected and observed in gas phase studies,³⁵ matrix investigations have invariably exhibited three optical bands.²⁹⁻³⁴ Initially ascribed to a distorted site (D_3 or D_4) splitting,^{34,36} this triplet is now known to arise from the Jahn-Teller (JT) splitting of the 3/2 (U' in O symmetry) component. Figure 1 shows the situation schematically. For the atomic species whose intrinsic SO splitting is very large (e.g. Au) the SO constant may be extracted³⁴ from the absorption spectral data using (cf. Fig. 1)

$$\zeta = 2/3[1/2(T_2 + T_3) - T_1] \quad (1)$$

But for atomic species whose intrinsic SO coupling is not very large and may be of the same order of magnitude as the JT splitting, it is necessary to use an MCD/absorption moment analysis approach.^{25,37}

Figure 1

Energy Level Diagram for an Alkali or Noble Metal
Atom in the Gas Phase and in Matrices
S.O. = Spin-Orbit, J.T. = Jahn-Teller



The ratio of the first MCD moment, $\langle \Delta A \rangle_1$, to the zeroth absorption moment, $\langle A \rangle_0$, is

$$\langle \Delta A \rangle_1 / \langle A \rangle_0 = 2(g - \zeta/2kT)\mu_B B \quad (2)$$

where g is the orbital g factor of the excited state, μ_B is the Bohr magneton and B is the magnetic field strength. The SO coupling constant, ζ , may be obtained from the slope of a plot of the moment ratio vs. $1/T$. In Table 1 are collected the experimentally observed SO constants for a few metal-rare gas systems. Here the trends referred to in the introduction can easily be discerned.

To understand the trend in Cu the initial approach²⁹ was to use the theory developed by Ammeter and Schlosnagle.³⁸ By orthogonalizing the metal atomic orbitals to the rare gas orbitals, they derived the following expression for the SO reduction factor

$$k = 1 - 4\zeta_X/\zeta_M(2S_\sigma S_\pi - S_\pi^2) \quad (3)$$

Table 1
Experimental Spin-Orbit Coupling Constants and Spin-Orbit
Reduction Factors for Selected Metals Representative of the
Three Major Categories

<u>Medium</u>	<u>Metal Atoms</u>					
	Cu ^a		Au ^b		Li ^c	
	ζ/cm^{-1}	k	ζ/cm^{-1}	k	ζ/cm^{-1}	k
Gaseous	166	--	2543	--	0.23	--
Ar	124	0.75	3215	1.26	-16	-70
Kr	95	0.57	2943	1.16	-70	-304
Xe	-23	-0.14	2570	1.01	-196	-852

a Ref. 25,26.

b Ref. 30.

c Ref. 27,28.

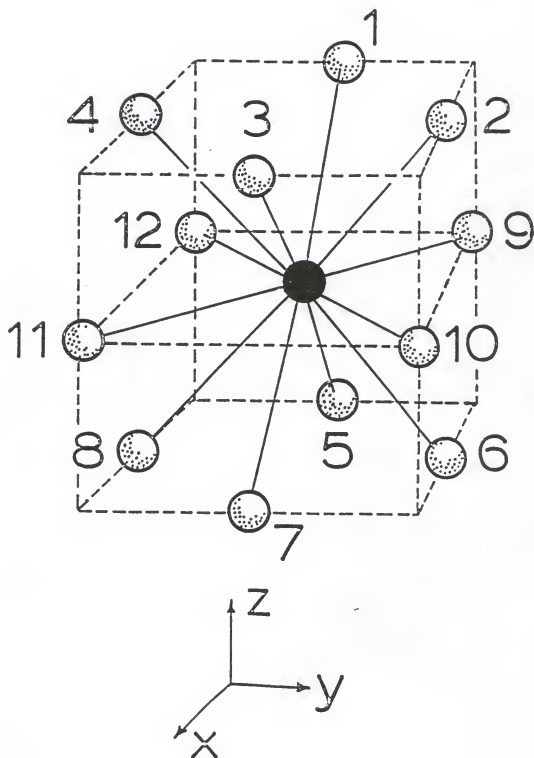
where the S_{σ} and S_{π} refer to σ and π type overlap integrals and the ζ_X and ζ_M are the rare gas and metal SO constants, respectively. Previous results,^{29,30} though dependent to some degree on the radial extent of the excited state Cu 4p orbital, correctly mimicked the downward trend (from Ar to Xe) and the negative sign for Xe. However, if one attempts to apply this same expression to the Au results,³⁴ the experimentally observed SO reduction factors with $k > 1$ cannot be reproduced. Since $2S_{\sigma}S_{\pi} > S_{\pi}^2$, the calculated reduction factors are all necessarily less than one. Because of this situation, this model was abandoned and another sought. In the simple model proposed here, it is shown that all of the major trends are predictable, and that they are dependent simply upon the metal-rare gas overlap integrals, the relative magnitudes of the metal and rare gas SO constants, and the metal-rare gas MO mixing coefficients.

Theoretical Approach

The supermolecule model used here assumes that the metal atom (M) resides in a tetradecahedral substitutional site composed of a first shell cage of twelve rare gas atoms (X). The supermolecule formula is therefore MX_{12} , cf. Fig. 2. This model has experimental validity for at least one metal-rare gas combination.

Figure 2

Supermolecule MX_{12} : Geometrical Arrangement for a Metal
Atom M (Black Sphere) Embedded in a Tetradecahedral
Substitutional Site of Rare Gas Atoms X (Open Spheres).



Kasai and McLeod have demonstrated ³⁹ that the superhyperfine splitting of the Cu ²S ground state ESR signal is due to the Xe matrix atoms arranged in a tetradecahedral substitutional site.

Basis Functions

The basis set consists of the metal atom excited state p orbitals plus the excited state rare gas (n + 1)p orbitals. The metal atom p orbitals (of t_{1u} symmetry in O_h) mix with the three sets of t_{1u} rare gas cage group orbitals. The cage group orbitals are given in Table 2 and their z components illustrated in Figure 3. (The y and z components are identical to within a rotation.) Using these components the LCAO supermolecular orbitals are

$$\phi_{t_{1u}}(x) = c_1 p_x^M + c_2 t_{1u}^1(x) + c_3 t_{1u}^2(x) + c_4 t_{1u}^3(x)$$

$$\phi_{t_{1u}}(y) = c_1 p_y^M + c_2 t_{1u}^1(y) + c_3 t_{1u}^2(y) + c_4 t_{1u}^3(y) \quad (4)$$

$$\phi_{t_{1u}}(z) = c_1 p_z^M + c_2 t_{1u}^1(z) + c_3 t_{1u}^2(z) + c_4 t_{1u}^3(z)$$

Table 2

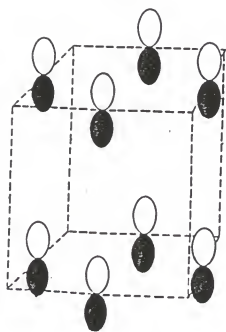
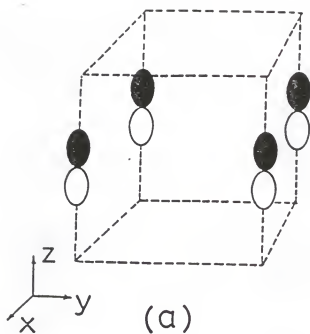
Rare Gas Atom Group Orbitals of the MX_{12} Supermolecule

<u>Designation</u>	<u>Group Orbital</u>
$t_{1u}^1(x)$	$x_2 + x_3 + x_6 + x_8$
$t_{1u}^1(y)$	$y_1 + y_3 + y_5 + y_7$
$t_{1u}^1(z)$	$z_9 + z_{10} + z_{11} + z_{12}$
$t_{1u}^2(x)$	$-(x_1 + x_3 + x_5 + x_7 + x_9 + x_{10} + x_{11} + x_{12})$
$t_{1u}^2(y)$	$-(y_2 + y_4 + y_6 + y_8 + y_9 + y_{10} + y_{11} + y_{12})$
$t_{1u}^2(z)$	$-(z_1 + z_2 + z_3 + z_4 + z_5 + z_6 + z_7 + z_8)$
$t_{1u}^3(x)$	$z_1 - z_3 - z_5 + z_7 + y_9 - y_{10} + y_{11} - y_{12}$
$t_{1u}^3(y)$	$-z_2 + z_4 + z_6 - z_8 + x_9 - x_{10} + x_{11} - x_{12}$
$t_{1u}^3(z)$	$x_1 - x_3 - x_5 + x_7 - y_2 + y_4 + y_6 - y_8$

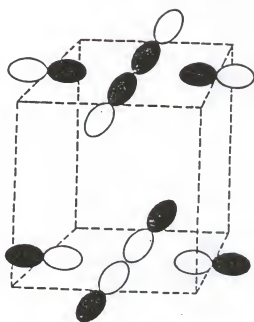
Figure 3

Schematic of the z Components of the Three t_{1u}
Rare Gas Atom Group Orbitals of the MX_{12}
Supermolecule.

- a) $t_{1u}^1(z)$ orbital
- b) $t_{1u}^2(z)$ orbital
- c) $t_{1u}^3(z)$ orbital



(b)



(c)

Here the superscripts M, 1, 2, 3 refer to the metal and different rare gas group orbitals, respectively. The c_i are the mixing coefficients.

These space orbitals may now be combined with either α or β spin functions and the resulting spin MOs used to construct a 6 X 6 SO matrix.

Spin-Orbit Matrix

The elements of the SO matrix have the form

$$\langle \phi_{tlu}(i)\sigma | H_{SO} | \phi_{tlu}(j)\sigma' \rangle \quad (5)$$

where $\sigma, \sigma' = \alpha$ or β spins and $i, j = x, y, \text{ or } z$. The SO operator is

$$H_{so} = \zeta_M \vec{l}_M \cdot \vec{s} + \zeta_X \sum_k \vec{l}_k \cdot \vec{s} \quad (6)$$

where ζ_M and ζ_X are the metal and rare gas SO coupling constants, respectively. The sum is over all rare gas atom centers. Making use of the standard angular momentum operator relations,² e.g. $s_x|\alpha\rangle = \hbar|\beta\rangle/4\pi$, $s_y|\alpha\rangle = i\hbar|\beta\rangle/4\pi$, $l_x p_y = i\hbar p_z/2\pi$, etc. and retaining only single center orbital angular momentum terms, the following SO matrix is found

$$A = \begin{bmatrix} 0 & 0 & 0 & -1 & 0 & i \\ 0 & 0 & 1 & 0 & i & 0 \\ 0 & 1 & 0 & 0 & -i & 0 \\ -1 & 0 & 0 & 0 & 0 & i \\ 0 & -i & i & 0 & 0 & 0 \\ -i & 0 & 0 & -i & 0 & 0 \end{bmatrix} \quad (7)$$

where

$$A = \hbar^2 (c_1^2 \zeta_M - 4c_1 c_2 \zeta_X S_1 - 4c_1 c_3 \zeta_X S_\pi + 4c_1 c_3 \zeta_X S_1 - 4c_1 c_4 \zeta_X S_2 + 4c_1 c_2 \zeta_M S_\pi + 8c_1 c_3 \zeta_M S_1 + 8c_1 c_4 \zeta_M S_2) / 8\pi^2 \quad (8)$$

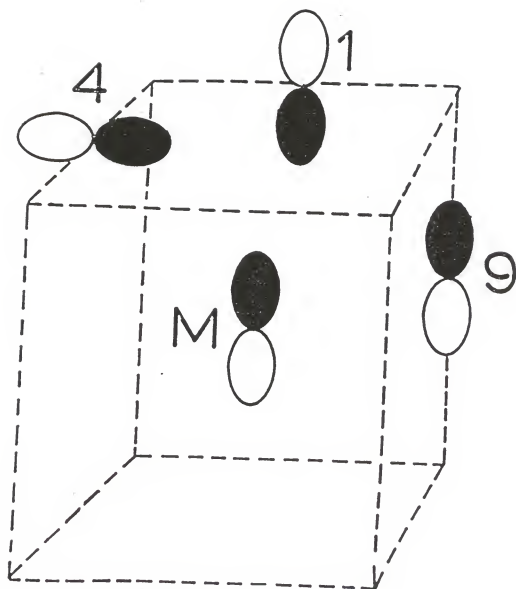
and $S_1 = \langle p_z^M | -z_1 \rangle$, $S_2 = \langle p_z^M | -y_2 \rangle$, and $S_\pi = \langle p_z^M | z_9 \rangle$. These overlap integrals are pictured in Figure 4.

Spin-Orbit Splitting and Reduction Factor

The above SO matrix has the same structure as the free atom ^2P SO matrix; for the free atom case $c_1 = 1$ and c_2, c_3 , and $c_4 = 0$ and A is equal to $\hbar^2 \zeta_M / 8\pi^2$.

Figure 4

Pictorial Representation of the Overlap Integrals
 S_1 (Between Atoms M and 1), S_2 (Between Atoms M and 4)
and S_π (Between Atoms M and 9).



Expanding the corresponding determinant and solving the characteristic equation leads to the eigenvalues, $E_1 = A$ (fourfold degenerate) and $E_2 = -2A$ (doubly degenerate). Thus spin-orbit coupling in the excited ^2P ($^2T_{1u}$) state results in a splitting (3A) with one multiplet (U' in O, $J= 3/2$ in the free atom) lying at $+A$ and the other (E' in O, $J= 1/2$ in the free atom) at $-2A$. In analogy to the free atom case, the splitting between these components is defined by

$$\Delta E = E_1 - E_2 = 3A \equiv 3\zeta_{\text{Eff}}h^2/8\pi^2 \quad (9)$$

The spin-orbit reduction factor, k , is defined as

$$k \equiv \zeta_{\text{Eff}}/\zeta_M = c_1^2 + 4c_1c_2S_\pi + 8c_1c_3S_1 + 8c_1c_4S_2 - 4c_1c_2S_1Q - 4c_1c_3S_\pi Q + 4c_1c_3S_1Q - 4c_1c_4S_2Q \quad (10)$$

where $Q = \zeta_X/\zeta_M$. This expression for k shows that the magnitude and sign of the metal atom SO splitting and its dependence on the rare gas originates in three quantities: the mixing coefficients (c_i), the overlap integrals (S_i), and the ratio of the rare gas to metal SO coupling constants (Q).

Overlap Integrals and SO Coupling Ratios

Following Burdett,⁴⁰ the S_1 and S_2 overlaps are easily obtained as

$$\begin{aligned} S_1 &= (S_\sigma - S_\pi)/2 \\ S_2 &= (S_\sigma + S_\pi)/2 \end{aligned} \tag{11}$$

where S_σ and S_π are the standard two center $p\sigma$ and $p\pi$ overlap integrals. To evaluate these integrals numerically for the various metal/rare gas combinations, available Slater basis functions for the np rare gas orbitals were used.⁴¹ The $(n + 1)p$ rare gas orbitals would have been preferred, but to the best of our knowledge, they are unavailable. Similarly, wavefunctions for the ground state unoccupied metal valence np orbitals are also not available. Exponents and coefficients for the valence ns orbitals of the metals were used instead.⁴¹ The known⁴² rare gas interatomic separations and the overlaps computed using them are given in Table 3.

Table 3

Metal-Rare Gas Overlaps and Spin-Orbit Constant Ratios

System		Interatomic				
Metal	Rare Gas	Separation ^a	S_{σ}	S_{π}	R	Q
Cu	Ar	7.098	0.1069	0.03168	3.374	5.687
	Kr	7.541	0.1147	0.03160	3.628	20.96
	Xe	8.193	0.1181	0.03059	3.862	36.63
Ag	Ar	7.098	0.1209	0.03621	3.339	1.564
	Kr	7.541	0.1307	0.03604	3.626	5.668
	Xe	8.193	0.1355	0.03461	3.914	9.902
Au	Ar	7.098	0.1279	0.03679	3.475	0.370
	Kr	7.541	0.1384	0.03623	3.821	1.368
	Xe	8.193	0.1428	0.03415	4.183	2.391
Li	Ar	7.098	0.1252	0.04176	2.998	4.1×10^3
	Kr	7.541	0.1367	0.04204	3.252	15×10^3
	Xe	8.193	0.1451	0.04131	3.512	26×10^3
Na	Ar	7.098	0.1301	0.04682	2.779	82.02
	Kr	7.541	0.1444	0.04777	3.023	303.7
	Xe	8.193	0.1560	0.04752	3.283	531.1
K	Ar	7.098	0.1308	0.06131	2.133	24.43
	Kr	7.541	0.1524	0.06449	2.363	90.43
	Xe	8.193	0.1752	0.06665	2.629	158.2

a Ref. 39; atomic units

b $R \equiv S_{\sigma}/S_{\pi}$ c $Q \equiv \zeta_X/\zeta_M$

It is interesting to note that for any one metal with the three rare gases the overlaps of a particular type are practically constant (e.g., for Cu/RG, $S_{\pi} \approx 0.031$ and $S_o \approx 0.11$). Also given in Table 3 are the rare gas to metal SO coupling constant ratios, Q . All of the SO constants were obtained from the relation

$$\zeta = 2\Delta E/3 \quad (12)$$

where $\Delta E = E(J=3/2) - E(J=1/2)$ for the metal np^1 electronic configuration⁴³ and $\Delta E = E(^3P_0) - E(^3P_2)$ for the rare gas $np^5(n+1)s^1$ configuration.^{44,45} Spectroscopic energies were taken from Moore's tables.³⁵

Mixing Coefficients

The remaining obstacle to obtaining a parameter-free theory for the SO splitting of metals in rare gas matrices is the estimation of the mixing coefficients (c_i , $i = 1 - 4$). Although a "complete" energy calculation on the MX_{12} supermolecule could have been attempted, we adopt a number of simplifying approximations here. First, it is assumed that the rare gas mixing coefficients (c_2 , c_3 , and c_4) are proportional to their respective metal atom-rare gas orbital overlaps

$$\begin{aligned}
 c_2 &\propto S_{\pi} \\
 c_3 &\propto S_1 = (S_{\sigma} - S_{\pi})/2 \\
 c_4 &\propto S_2 = (S_{\alpha} + S_{\pi})/2
 \end{aligned} \tag{13}$$

and that the metal atom coefficients, $c_1 \approx 1$. It is then possible to express two of the above rare gas coefficients as a function of the third. Let $c = c_2$ and $R = S_{\sigma}/S_{\pi}$ (cf. Table 3); then $c_3 = (R - 1)c/2$ and $c_4 = (R + 1)c/2$. Thus the evaluation of three mixing coefficients has been reduced to the estimation of only one, c .

Insertion of (11) and the expressions above for c_2, c_3 , and c_4 into (10) yields after simplification

$$k = 1 + 4cS_{\pi}(2R - 1)((R^2 + 2)/(2R - 1) - Q) \tag{14}$$

This expression is the master equation of the present theory. It is instructive to analyze this expression briefly to determine whether the three major classes of spin-orbit reduction factors may be predicted from it. These classes are I) $k > 1$ (i.e., SO constants $>$ than gas phase values), II) $0 < k < 1$ (SO constants positive and less than gas phase values), and III) $k < 0$ (SO constants negative and less than gas phase values). The pivotal factor in expression (14) above is the quantity in square brackets, that is, the relative

magnitudes of the ratio $(R^2 + 2)/(2R - 1)$ and the ratio Q ($\equiv \zeta_X/\zeta_M$). The former depends solely on the ratio of overlap integrals ($R = S_\sigma/S_\pi$) while the latter is simply the ratio of rare gas and metal SO coupling constants. The limiting conditions under which the three classes may be expected are simply stated. They are I) for $(R^2 + 2)/(2R - 1) > Q$, k will be greater than 1, II) for $(R^2 + 2)/(2R - 1) < Q$, k will fall between 0 and 1, and III) for $(R^2 + 2)/(2R - 1) \ll Q$, k will be less than 0. The numerical values for the ratio $(R^2 + 2)/(2R - 1)$ for the metal-rare gas combinations studied here are presented in Table 4. Interestingly, the ratio is practically constant (and equal to $\approx 2.3 \pm 0.3$) for any combination of one metal with the rare gases. This is, of course, a reflection of the fact noted above that S_σ and S_π do not vary substantially from one combination to the next. Thus, the assignment of a certain metal-rare gas combination to a particular SO reduction factor class (I, II, or III) is primarily dependent upon Q .

In Table 4 are listed two Q values for each metal-rare gas combination. The first, labelled Q_{np} , uses the well-known rare gas SO constant (ζ_X) for the $np^5(n+1)s^1$ configuration obtained from the lowest excited ^3P state. The predicted classes, labelled np , are also in the table.

It can be seen that all 3 classes are predicted and, where experimental data are available, are in good accord. For 2 cases (Cu/Kr and K/Ar) some ambiguity exists since the crossover point from class II to class III is not well defined (since it depends upon the factor $4cS_n$).

The second Q , labelled Q_{ave} , is an energy-weighted average of Q_{np} and $Q_{(n+1)p}$, the latter obtained using $\zeta_{(n+1)p}$ for the rare gas $np^5(n+1)p^1$ configuration. The rationale for using an average Q and its definition are given in the next section after a description of the terms which comprise it. The predicted classes (labelled ave) using this Q are also given in Table 4. In this case the predicted classes for the alkalis and gold are the same as above. The Ag/Kr prediction is now class I and Ag/Xe class I or II. The only discrepancy with experimental observation is for Cu/Ar which is predicted to be class I and is known to be class II. Despite this, we conclude that the present model is capable of predicting qualitatively the major features of the S_0 coupling of metals in rare gas matrices.

Quantitative Estimation of S_0 Reduction Factors

We next turn to a quantitative estimation of the mixing coefficient (c) and thence to the numerical prediction of the S_0 reduction factors. To calculate c , a perturbation approach, as outlined schematically in Figure 5, is adopted.

Table 4

Metal-Rare Gas Overlap Ratios, Spin-Orbit Constant Ratios
and Predicted and Experimental Reduction Factor Classes

System	R^a	$\frac{R^2+2}{2R-1}$	Q_{np}^b	Predicted ^C Class(np)	Q_{Ave}^b	Predicted ^C Class(Ave)	Exper. Class	Ref
Cu/Ar	3.374	2.328	5.687	II	.998	I	II	29,30
Cu/Kr	3.628	2.424	20.96	IIorIII	4.172	II	II	29,30
Cu/Xe	3.862	2.516	36.63	III	8.883	III	III	29,30
Ag/Ar	3.339	2.316	1.564	I	0.263	I		
Ag/Kr	3.626	2.423	5.668	II	1.089	I		
Ag/Xe	3.914	2.536	9.902	II	2.324	I or II		
Au/Ar	3.475	2.366	0.370	I	0.074	I	I	34
Au/Kr	3.821	2.499	1.368	I	0.311	I	I	34
Au/Xe	4.183	2.647	2.391	I	0.659	I	I	34
Li/Ar	2.998	2.199	4100	III	611.8	III	III	31,32
Li/Kr	3.252	2.285	15000	III	2543	III	III	31,32
Li/Xe	3.512	2.380	26000	III	5422	III	III	31,32
Na/Ar	2.779	2.133	82.02	III	9.364	III		
Na/Kr	3.023	2.207	303.7	III	39.05	III		
Na/Xe	3.283	2.296	531.1	III	85.38	III	III	32
K/Ar	2.133	2.005	24.43	IIorIII	2.253	II	II	32,33
K/Kr	2.363	2.035	90.43	III	9.397	III	III	32,33
K/Xe	2.629	2.093	158.2	III	20.90	III	III	32,33

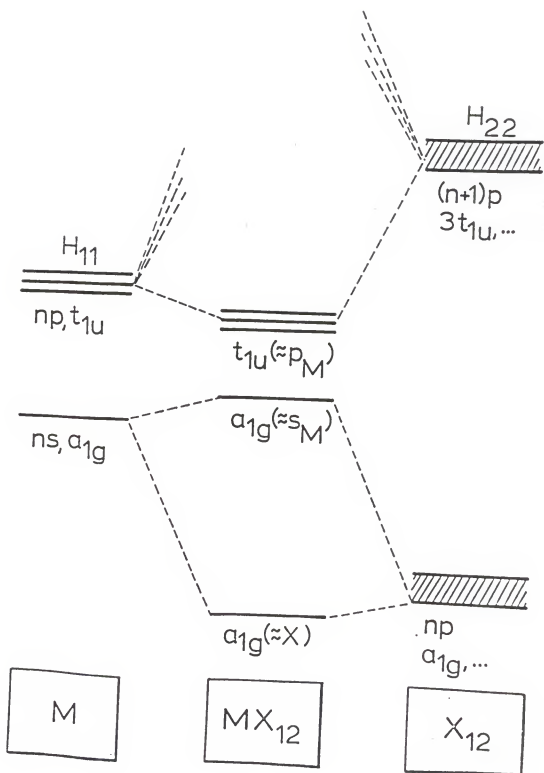
a $R \equiv S_o/S_\pi$

b $Q \equiv \zeta_X^o/\zeta_M^\pi$

c Class I: $k>1$; Class II: $0<k<1$; Class III: $k<0$

Figure 5

Orbital Perturbation Scheme for the Interaction of
the Metal p Orbitals with the Rare Gas (n+1)p
Group Orbitals.



Here "1" is a metal valence p orbital of energy H_{11} and "2" is a rare gas $(n + 1)p$ orbital of energy H_{22} . Note that the $(n + 1)p$ unoccupied orbitals, not the occupied np orbitals, are chosen to interact with the excited metal p electron. The major reason for this choice is the closer proximity of the p metal and $(n + 1)p$ rare gas orbitals (measured for the ionization limit as zero) compared to the p metal and np rare gas orbitals. For example, the H_{22} energy of the 4p orbital of Ar lies at -2.588 eV compared to -15.76 eV (127109.9cm^{-1}) for the 3p Ar orbital. The 2p orbital of Li lies at -3.543 eV (H_{11} , cf. Table 6,7) with all the other metal p orbitals lying within ± 0.8 eV of this value. Another reason for choosing the $(n + 1)p$ orbital is that for the rare gases in their ground states it is unoccupied and is able to accept electron density from the metal p orbital, thereby facilitating the metals' interaction with the rare gas cage.

In the spirit of the Wolfsberg-Helmholtz approximation,⁴⁰ the interaction Hamiltonian is assumed to have the form

$$H_{12} = (H_{11} + H_{22})S_{12} \quad (15)$$

Solution of the secular equation yields

$$E_{\pm} = \{H_{11} + H_{22} - 2(H_{11} + H_{22})S_{12}^2 \pm [(H_{11} - H_{22})^2 + 4H_{11}H_{22}S_{12}^2]^{.5}\}/2(1 - S_{12}^2) \quad (16)$$

from which c may be obtained as

$$c = [(H_{22}/(E_- - H_{11}) - 1)S_{12}]^{-1} \quad (17)$$

The H_{11} and H_{22} energies are computed with atomic spectroscopic data from Moore³⁵ using the following expressions

$$H_{11} = (2E_{1/2}^M + 4E_{3/2}^M)/6 - E_{\text{Ion}}^M \quad (18)$$

$$H_{22} = \sum_i (2J_i + 1)E_i^X/36 - E_{\text{Ion}}^X$$

The specific energy values used are given in Tables 5 and 6. The first term on the RHS is the weighted average excitation energy for the transition $ns^1 \rightarrow np^1$ (metal) or $np^6 \rightarrow np^5(n+1)p^1$ (rare gas). Subtracting the ground state ionization energies from these averaged energies and applying Koopman's theorem^{46,47} gives approximate values for the desired orbital energies. These are tabulated in Table 7 along with the computed mixing coefficients. (Note that in this calculation $S_{12} = S_{\pi}$ due to the way in which c was defined.)

Before evaluating the SO reduction factors, it is necessary to present the rationale for using a Q (and hence ζ_X) other than Q_{np} .

Table 5
 Experimental Energies³² Used to Calculate H_{11} for an
 np^1 Configuration

<u>Metal</u>	<u>n</u>	Energies/cm ⁻¹		Ionization Energy/cm ⁻¹
		<u>J = 1/2</u>	<u>J = 3/2</u>	
Li	2	14903.66	14904.00	43487.19
Na	3	16956.183	16973.379	41449.65
K	4	12985.17	13042.89	35009.78
Cu	4	30535.302	30783.686	62317.2
Ag	5	29552.05	30472.71	61106.50
Au	6	37358.9	41174.3	74410.0

Table 6
Experimental Energies³² (cm^{-1}) Used to Calculate H_{22} for
an $(n + 1)p^1$ Configuration

		<u>Rare Gas</u>		
<u>Configuration</u>	<u>J</u>	<u>Ar(n = 3)</u>	<u>Kr(n = 4)</u>	<u>Xe(n = 5)</u>
$np^5(n + 1)p^1$	1	104102.144	91169.313	77269.649
	3	105462.804	92295.197	78120.303
	2	105617.315	92308.177	78403.562
	1	106087.305	92965.194	78956.538
	2	106237.597	93124.140	79212.970
	0	107054.319	94093.662	80119.474
$np^5(n + 1)p^1$	1	107131.755	97596.718	88379.647
	2	107289.747	97945.970	89162.880
	1	107496.463	97919.951	89279.233
	0	108722.688	98855.871	89860.538
Ionization Energy		127109.9	112915.2	97834.4

Table 7

Empirical Orbital Energies for Metals (H_{11}) and Rare Gases (H_{22}) Computed Mixing Coefficients (c) and SO Reduction Factors (k)

System		$-H_{11}$	$-H_{22}$				
Metal/Rare Gas		(ev)	(ev)	c	k_{np}	k_{ave}	k_{exp}
Cu	Ar	3.919	2.588	0.0612	0.85	1.06	0.75 ^a
	Kr	3.919	2.307	0.0451	0.34	0.94	0.57 ^a
	Xe	3.919	1.959	0.0305	0.14	0.84	-0.14 ^a
Ag	Ar	3.835	2.588	0.0745	1.05	1.13	
	Kr	3.835	2.307	0.0542	0.84	1.07	
	Xe	3.835	1.959	0.0361	0.75	1.01	
Au	Ar	4.277	2.588	0.0561	1.06	1.11	1.26 ^b
	Kr	4.277	2.307	0.0399	1.05	1.09	1.16 ^b
	Xe	4.277	1.959	0.0288	1.01	1.06	1.01 ^b
Li	Ar	3.543	2.588	0.1113	-380	-55.6	-70 ^c
	Kr	3.543	2.307	0.0777	-1.08×10^3	-181.8	-304 ^c
	Xe	3.543	1.959	0.0509	-1.32×10^3	-273.4	-852 ^c
Na	Ar	3.035	2.588	0.2510	-16.1	-0.55	
	Kr	3.035	2.307	0.1471	-41.8	-4.22	
	Xe	3.035	1.959	0.0855	-46.9	-6.52	-18.6 ^d
K	Ar	2.725	2.588	0.6473	-10.6	+0.87	>0 ^e
	Kr	2.725	2.307	0.3144	-25.7	-1.22	<0 ^e
	Xe	2.725	1.959	0.1641	-28.1	-2.50	-.42 ^e

a. Ref. 25,26.

d. Ref. 28.

b. Ref. 30.

e. Ref. 28,29.

c. Ref. 27,28.

The ζ_X used in Q_{np} is not entirely appropriate since the overlaps described in the present theory are between the $(n + 1)p$ orbitals, not the np orbitals, of the rare gas and the p orbital of the metal. This is diagrammed in Figure 5. The interaction of the metal p orbital will be primarily with the rare gas $(n + 1)p$ orbitals due to their energetic proximity. To account for this twofold interaction, we have taken an energy weighted average of the Q_{np} and $Q_{(n + 1)p}$. The expression used is

$$Q_{Ave} = (E_{Ion}^X + H_{11})Q_{(n + 1)p} / (E_{Ion}^X + H_{22}) + (H_{22} - H_{11})Q_{np} / (E_{Ion}^X + H_{22}) \quad (19)$$

where E_{Ion}^X is the ionization energy of the rare gas. The ζ_X used for the $Q_{(n + 1)p}$'s are taken from Ref. 2 with the unknown value for Ar interpolated from the other rare gas values.

The SO reduction factors may now be evaluated using (14). This has been done using the two sets of Q discussed above. The k so obtained are labelled k_{np} and k_{ave} and are given in Table 7, together with a listing of the experimental values, k_{exp} , where known.

Discussion

Confining our discussion initially to the k_{np} results, it can be seen from Table 7 that most of the trends noted in the

Introduction are predicted by the present supermolecule approach. That is, 1) k and hence ζ_{Eff} for all metals decrease in the order $\text{Ar} > \text{Kr} > \text{Xe}$, 2) the k for Au are all greater than one, indicating that its SO constant is greater in matrices than in the gas phase, and 3) the alkali metal k reported to date are predicted to be negative in all the rare gases (i.e. the U' ($J = 3/2$) state lies below the E' ($J = 1/2$) state; c.f. Fig. 1).

While encouraging, the results for k_{np} are not without some problems, the major of which is the failure to predict a negative k for Cu/Xe. We postpone discussion of this point until after presentation of the k_{ave} results. Another problem arises in the predictions for the alkali metals. Although all are of the correct sign, the predicted magnitudes are too large by factors in the range 2 - 9. Perhaps because of their smaller size relative to the noble metals, the alkalis (particularly Li and Na) may occupy sites other than the twelve-coordinate tetradecahedral one assumed here. In Appendix A it is shown that the SO reduction factor expression for a six coordinate octahedral site is identical to (14) except that the numerical coefficient in the second term is 2 instead of 4. Therefore, occupation of a six or possibly four coordinate site would improve our prediction by a factor of 2 or 3, respectively. This is however not sufficient to bring theoretical and experimental k values into agreement. The k_{np} predictions are based on Q_{np} values found using ζ_{np} constants for the $\text{np}^5(n+1)\text{s}^1$ electronic configuration.

If, however, the ζ_x for the $(n + 1)p^1$ configuration are used, smaller SO constants are expected because of the screening effect associated with the larger principal quantum number.² Q should then be smaller and the predicted k 's more in line with experiment. This is in fact the case. However, rather than report the k computed from these $Q_{(n + 1)p^1}$, we choose instead to give the k_{ave} which provide better overall results. Table 7 shows that the k predicted for the alkalis are much reduced and indeed are now of the correct order of magnitude. The Li/Ar prediction is now within $\approx 20\%$ of the observed value and, significantly, the K/Ar prediction is now just positive, in accord with experiment. For the alkalis, as the rare gas atomic number increases, the agreement with experiment seems to worsen. However, the K/Xe result is less than a factor of two from the experimental value. This probably reflects the fact that Li and Na fit most snugly into the Ar substitutional MX_{12} site, whereas K fits best into Xe. The relevant covalent radii are given in Table 8. For the noble metals, the predictions are good except for Cu. The prediction for Ag is now that the k 's for all the rare gases will be greater than one, as in Au.

The Cu results are perplexing for several reasons. First, the Cu/Ar k is now greater than one, contrary to experiment, and secondly, the Cu/Xe k is not negative, as observed. In the case of this metal only, the prediction using k_{ave} is poorer than using k_{np} . Interestingly, of all the six metals studied here Cu has the smallest atomic radius (1.28Å, cf. Table 8). Indeed it is

more than 30% smaller than even Ar. It could be that because of its small size the matrix cage collapses around the Cu as the matrix isolation process proceeds. To test the effect of such a collapse, the interatomic distances in the Cu-rare gas cage were reduced by 25% and new overlap integrals and mixing coefficients computed. From them, new k_{ave} 's were determined. The results are shown in Table 9. The k from Cu/Xe is now negative as observed and the k for Cu/Kr is in good agreement with experiment. (For a 27% decrease, the Cu/Xe k becomes -0.17.) The Cu/Ar result remains greater than one however. This highlights an important feature of expression (14). The major effect of the recalculation of overlap integrals and mixing coefficients due to interatomic distance changes or changes in the radial portion of the wavefunctions employed will be on the coefficient in front of the term in square brackets (i.e. , $4cS_{\pi}(2R - 1)$). Of the terms within the square bracket, the ratio $(R^2 + 2)/(2R - 1)$ changes little and Q not at all. This means that those metal-rare gas combinations in Class I will remain in Class I and their k values will become larger. For those combinations in Class II, since the quantity in square brackets is negative, a larger coefficient in front will decrease the k value and may even cause it to become negative.

Table 8

Atomic Covalent Radii for the Noble and Alkali
Metals and the Rare Gases^a

<u>Atom</u>	<u>Atomic Radius/Å</u>	<u>Period</u>
Ar	1.90	3
Kr	2.00	4
Xe	2.20	5
Li	1.52	2
Na	1.85	3
K	2.31	4
Cu	1.28	4
Ag	1.44	5
Au	1.44	6

^a B. Douglas, D.H. McDaniel, and J.J. Alexander, Concepts and Models of Inorganic Chemistry, 2nd Ed., Wiley and Sons, New York, 1983.

Table 9

Overlap Integrals, Mixing Coefficients, and SO Reduction Factors for Cu and the Rare Gases with 25% Collapsed Lattice

<u>System</u>					
Metal	Rare Gas	S_{σ}^a	S_{π}^a	c	k_{ave}^b
Cu	Ar	0.2033	0.09344	0.1734	1.220
	Kr	0.2267	0.09830	0.1363	0.585
	Xe	0.2462	0.10037	0.0984	-0.054

^a Calculated for a 25% decrease in the metal to rare gas atom distance.

^b Computed using Q_{ave} , cf. Table 4.

And for Class III combinations, their k will become more negative. so the discrepancy in the Cu/Ar value cannot be corrected by using better wavefunctions or more accurate cage dimensions. It most likely results from the Q_{ave} used. $Q_{(n+1)p}$ for Cu/Ar is 0.471 which leads to a $k = 1.08$ (with no lattice contraction). Apparently in this case the Cu p orbital interactions with the Ar np orbitals are greater than accounted for by the expression for Q_{ave} . Using Q_{np} alone yields a k value (0.85) in good agreement with experiment (0.75).

Conclusion

Three classes of spin-orbit splitting in the excited $2p$ states of alkali and noble metals in rare gas matrices have been recognized. They comprise values which are (I) positive and greater than gas phase values, (II) positive and smaller than gas phase values and (III) negative and smaller than gas phase values.

To account theoretically for these classes a supermolecule model of the metal in the matrix is proposed. The model assumes that only the first shell of rare gas atoms is important and that the supermolecule is composed of a metal in a substitutional site surrounded by twelve rare gas atoms. The relevant MOs are formed using metal p orbitals and rare gas $(n+1)p$ orbital. The spin-orbit matrix is constructed using a Hamiltonian which includes one center SO operators on the metal and each rare gas atom.

Solution of the secular equation shows that the SO splitting in the matrix is dependent on three factors: the metal rare gas overlap integrals, the MO coefficients, and the relative magnitudes of the metal and rare gas SO coupling constants.

With some approximations, a simple master equation for the SO reduction factor is derived. It is shown that for certain limiting conditions this expression is capable of predicting the three major classes.

Quantitative estimates of the SO reduction factors for the noble and alkali metals in the rare gases, Ar, Kr, and Xe are made using a semiempirical approach. Two different sets of SO reduction factors are computed, the first (k_{np}) utilizing the rare gas SO coupling constants derived from the $np^5(n+1)s^1$ electronic configuration and the second (k_{ave}) involving an energy weighted average of the np and $(n+1)p$ SO constants. Both mimic the following experimental observations well: 1) decreasing k 's for all metals in the order $Ar > Kr > Xe$, 2) k 's for Au greater than one for all rare gases, and 3) alkali metal k 's all negative with the exception of K/Ar which k_{ave} predicts correctly but k_{np} does not. Both approaches have trouble with Cu, however. It is pointed out that a collapsed rare gas cage in this case is a reasonable possibility.

This work represents an attempt to account both qualitatively and quantitatively for the external heavy atom effect of noble and alkali metals in rare gas matrices.

A wide variety of experimental observations can be accounted for by this simple parameter-free theory. Extension of the present theory to other systems such as F centers or aromatic hydrocarbons would be interesting.

CHAPTER 3
MAGNETIC CIRCULAR DICHROISM OF ATOMIC RHENIUM IN A
KRYPTON MATRIX: LARGE GROUND STATE CRYSTAL FIELD SPLITTING

Introduction

Manganese and rhenium, as first and third row partners in group VII B, are expected to have the same electronic ground state in various media. Spectroscopic studies³⁵ show that both possess a $6S_{5/2}$ ground state in the vapor phase. Matrix studies of Mn concur with this assignment^{48,49} but a recent matrix study has called into question an analogous assignment for Re in argon matrices. Recently, Weltner and co-workers attempted to observe an ESR spectrum of Re in an Ar matrix but found no signal.⁴⁹ This surprising result led to several questions: Was the vapor phase work³⁵ in error in assigning the ground state to $6S_{5/2}$? Was there a matrix induced inversion of electronic states, as had recently been seen⁵⁰⁻⁵⁴ for Ni atoms in Ar, Kr, and Xe matrices? Or, was a large matrix-induced crystal field splitting of the $6S_{5/2}$ ground state responsible? There have been several other matrix studies on Re but they cast little light on this problem. Klotzbucher and Ozin have reported⁵⁵ the optical absorption spectrum (550-200 nm region) of Re matrix-isolated in Ar and, by comparison to vapor phase

results, tentatively assigned the observed bands. A $6s_{5/2}$ ground state was assumed by these authors. Ozin and Kundig⁵⁶ reported on the reactions of Re atoms isolated in a CO matrix.

Here we present the results of our magnetic circular dichroism (MCD)/absorption study of Re atoms isolated in a Kr matrix. To investigate the electronic ground state, use has been made of the MCD saturation method. This method, in which one or more optical transitions are monitored as a function of temperature and/or magnetic field strength, possesses the advantage that it may be used to probe paramagnetic samples, even though the sample may be ESR-silent. It is shown from the analysis of our MCD saturation results that a spin-orbit induced mixing of a low lying $4p_{5/2}$ state into the $6s_{5/2}$ ground state gives rise to a large matrix-induced zero field splitting. This splitting of 7.5 cm^{-1} is sufficient to preclude the observation of any X-band ESR spectrum at 4 K.

Initially, the theoretical expressions necessary to extract the crystal field splitting are developed. The spectral assignments and saturation results are then presented followed by a discussion of our findings.

Theory

Ground State Wavefunctions

The Re atom is assumed (1) to occupy a substitutional site of octahedral symmetry in the krypton matrix and (2) to have a ${}^6S_{5/2}$ ground state in this matrix. Since the ${}^6S_{5/2}$ state possesses only spin angular momentum and the crystalline electric field is spin independent, the state will not split to first order. When an appropriate orbital angular momentum bearing state is coupled to it, however, the ${}^6S_{5/2}$ state will split into E'' and U' (O symmetry) components. These components may be expanded in a $|J M_J\rangle$ basis as follows:

$$|G\sigma\rangle = \sum_{M_J} \Gamma_{G\sigma}(M_J) |5/2 M_J\rangle \quad (20)$$

where $|G\sigma\rangle$ stands for $E''\alpha$, $E''\beta$, $U'\kappa$, $U'\nu$, $U'\mu$, $U'\lambda$, and the coefficients $\Gamma_{G\sigma}(M_J)$ have been given by Griffith⁵⁸; they are tabulated in Table 10.

Mixing of the lowest lying excited state, the ${}^4P_{5/2}$ (located at 11584cm^{-1}), into the ${}^6S_{5/2}$ ground state may occur via spin-orbit coupling. While this state does possess orbital angular momentum, it is nonetheless insufficient to produce any ground state splitting.

Since a Re atom has a half filled ground state configuration, it is possible to group its d^5 Russell-Saunders terms into two classes bases upon their seniority quantum number (lower left hand index).

Class I	Class II
${}^2_1D$	${}^2_3PDFGH$
${}^2_5SDFGI$	${}^4_3PF$
${}^4_5DG$ ${}^6_5S$	

The only nonvanishing spin-orbit or crystal field matrix elements have the form $\langle \text{Class I State} | H | \text{Class II State} \rangle$; there are no diagonal matrix elements of these two operators for a half filled shell (viz. $\langle {}^4P | H_{CF} | {}^4P \rangle = \langle {}^6S | H_{CF} | {}^6S \rangle = 0$).

It is important to note that since the ground state has a nominal spin, $S = 5/2$, it cannot mix via the spin independent crystal field Hamiltonian with higher lying doublet ($S = 1/2$) and quartet ($S = 3/2$) states. Therefore, admixture of orbital angular momentum into the ground state occurs via states such as the ${}^4G$ (viz. $\langle {}^4P | H_{CF} | {}^4G \rangle$) which are crystal field coupled to the ${}^4P$ excited state. Hence we write for the ground state wavefunction

$$|5/2 M_J\rangle = \sum_{i=1}^{i=3} c_i |5/2 M_J, i\rangle \quad (21)$$

Table 10

Octahedral Symmetry Adapted Wavefunctions in the $|J M_J\rangle$
Basis for $J = 5/2^a$

O_h Label	Wavefunction
$ E''\alpha\rangle$	$[5/2 \ 5/2\rangle - \sqrt{5} 5/2 \ -3/2\rangle]/\sqrt{6}$
$ E''\beta\rangle$	$[5/2 \ -5/2\rangle - \sqrt{5} 5/2 \ 3/2\rangle]/\sqrt{6}$
$ U'\kappa\rangle$	$-[5/2 \ 3/2\rangle + \sqrt{5} 5/2 \ -5/2\rangle]/\sqrt{6}$
$ U'\lambda\rangle$	$ 5/2 \ 1/2\rangle$
$ U'\mu\rangle$	$ 5/2 \ -1/2\rangle$
$ U'\nu\rangle$	$[5/2 \ -3/2\rangle + \sqrt{5} 5/2 \ 5/2\rangle]/\sqrt{6}$

^a Reference 58.

where the 1, 2, and 3 subscripts and labels in the kets refer to the ${}^6S_{5/2}$, ${}^4P_{5/2}$, and ${}^4G_{5/2}$ states, respectively. The $|G\sigma\rangle$ wavefunctions may now be written

$$|G\sigma\rangle = \sum_{M_J} \Gamma_{G\sigma}(M_J) \left[\sum_i c_i |5/2 \ M_J, \ i\rangle \right] \quad (22)$$

Crystal Field and Zeeman Splitting

These wavefunctions can now be used to calculate the crystal field and Zeeman splitting. The Hamiltonian is

$$H = H_{CF} + H_B \quad (23)$$

where $H_{CF} = B_4(O_4^0 + 5O_4^4)$ and $H_B = g\mu_B J_z$. Here the crystal field Hamiltonian is expressed in terms of equivalent operators with the axis of quantization assumed to be along the crystalline site's fourfold axis. Similar results are obtained with the axis of quantization assumed to lie along the threefold axis.⁵⁹

Evaluating the matrix element $\langle G\sigma | H | G\sigma \rangle$ gives

$$\langle G\sigma | H | G\sigma \rangle = \sum_{M_J} \sum_{M_J'} \sum_i \sum_j \Gamma_{G\sigma}(M_J) \Gamma_{G\sigma}(M_J') c_i c_j \langle 5/2 \ M_J, i | H | 5/2 \ M_J', j \rangle$$

(24)

Using the octahedral component states given in Table 10, the Zeeman and crystal field matrix elements in Eq. (24) are readily evaluated. The results are given in Table 11. Due to the relatively small magnetic fields used here (0.5 T), the off diagonal Zeeman matrix elements $\langle E''\alpha | H_B | U'\nu \rangle$ and $\langle E''\beta | H_B | U'\kappa \rangle$ have been neglected. The results are sketched in Fig. 6 where it can be seen that the crystal field splitting is equal to $3A$. Here $A \equiv 240B_4C_2C_3$ and C_2 and C_3 represent the mixing coefficients of the ${}^4P_{5/2}$ and ${}^4G_{5/2}$ states, respectively. For a sufficiently large splitting no ESR transitions would be expected at low temperatures between the individual U' components or between the E'' and U' components. Transitions between the $E''\alpha$ and $E''\beta$ Kramer's doublet components are expected to be very weak, if observable at all.

Table 11

Crystal Field and Zeeman Matrix Elements for the ${}^6S_{5/2}$
Ground State Perturbed by the Nearby ${}^4P_{5/2}$ State

Ground State

Component

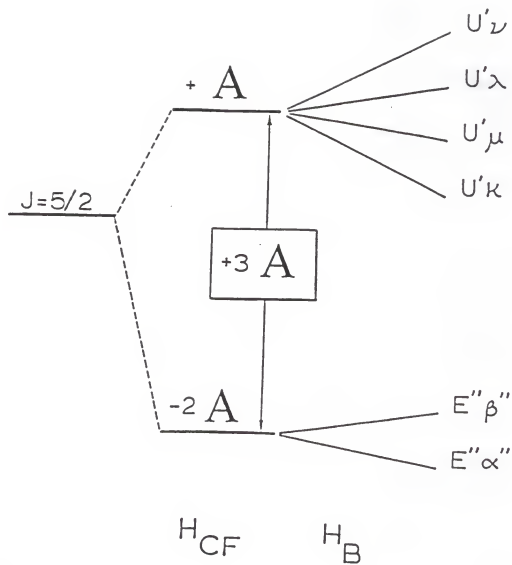
$\langle G\sigma | H_{CF} + H_B | G\sigma \rangle$

E^{α}	$-2A - 5/6(c_1^2 x_1 + c_2^2 x_2 + c_3^2 x_3)^a$
E^{β}	$-2A + 5/6(c_1^2 x_1 + c_2^2 x_2 + c_3^2 x_3)$
U^{κ}	$A - 11/6(c_1^2 x_1 + c_2^2 x_2 + c_3^2 x_3)$
U^{μ}	$A - 1/2(c_1^2 x_1 + c_2^2 x_2 + c_3^2 x_3)$
U^{λ}	$A + 1/2(c_1^2 x_1 + c_2^2 x_2 + c_3^2 x_3)$
U^{ν}	$A + 11/6(c_1^2 x_1 + c_2^2 x_2 + c_3^2 x_3)$

^a $x_1 \equiv g_1 \mu_B B$, where g_1 is the g factor for the ${}^6S_{5/2}$ state; $x_2 \equiv g_2 \mu_B B$, where g_2 is the g factor for the ${}^4P_{5/2}$ state; $x_3 \equiv g_3 \mu_B B$ where g_3 is the g factor for the ${}^4G_{5/2}$ state; the coefficients c_1 , c_2 , and c_3 are defined by Eq. (26) and the crystal field parameter $A \equiv 240B_4 c_2 c_3$ (+ higher terms).

Figure 6

Schematic Energy Level Diagram for a $J = 5/2$ State
Showing the Influence of a Crystal Field (H_{CF})
and a Magnetic Field (H_B).



MCD Saturation Expressions

The general expression for the differential absorbance (ΔA) observed in MCD is given by⁶⁰

$$\Delta A = qfcy/Z \sum_{\alpha} \sum_{\beta} \exp(-\langle A\alpha | H | A\alpha \rangle / kT) \times \quad (25)$$

$$[|\langle A\alpha | m_- | J\beta \rangle|^2 - |\langle A\alpha | m_+ | J\beta \rangle|^2]$$

where $\Delta A = A_- - A_+$, q is a constant, f is the bandshape function, c is the sample concentration, y the pathlength, and Z the electronic partition function. A denotes the ground electronic state with components α while J and β refer to the excited electronic state on which the optical transition terminates. The electric transition dipole operators are defined by $m_{\pm} \equiv (m_x \pm im_y)/\sqrt{2}$.

The transition moment matrix elements are easily evaluated using the Wigner-Eckart theorem.

$$|\langle G\sigma | m_{\pm} | J\beta \rangle|^2 = \left| \sum_{i=1} c_i \langle 5/2, i | m | J \rangle \right|^2 \times$$

(26)

$$\Gamma_{G\sigma}^{2(\beta \pm 1)} \begin{pmatrix} 5/2 & 1 & J \\ -\beta \mp 1 & \pm 1 & \beta \end{pmatrix}^2$$

Inserting Eq. (26) into Eq. (25), substituting $|G\sigma\rangle$ for $|A\alpha\rangle$ and factoring out the reduced matrix element term we find

$$\Delta A \propto (1/Z) \sum_{\sigma} \exp(-\langle G\sigma | H | G\sigma \rangle / kT) \times$$

(27)

$$\left[\Gamma_{G\sigma}^{2(\beta - 1)} \begin{pmatrix} 5/2 & 1 & J \\ -\beta + 1 & -1 & \beta \end{pmatrix}^2 - \Gamma_{G\sigma}^{2(\beta + 1)} \begin{pmatrix} 5/2 & 1 & J \\ -\beta - 1 & 1 & \beta \end{pmatrix}^2 \right]$$

Finally, substituting the CF/Zeeaman energies from Table 11 into Eq. (27) and computing the 3j coefficients,⁶¹ we obtain the following MCD saturation expression for the transitions $J = 5/2(E'', U') \rightarrow J = 3/2, 5/2, 7/2$.

$$\Delta A \propto \pm [5\exp(2A/kT)\sinh(5x/6) + \exp(-A/kT)(11\sinh(11x/6) + 3\sinh(x/2))]/Z \quad (28)$$

where

$$Z = 2[\exp(2A/kT)\cosh(5x/6) + \exp(-A/kT)(\cosh(11x/6) + \cosh(x/2))] \quad (29)$$

and $x \equiv (c_1^2 x_1 + c_2^2 x_2 + c_3^2 x_3)/kT$ with x_1 , x_2 and x_3 defined in Table 11. The plus sign holds for the cases $\Delta J = 0, -1$ while the negative sign applies to the $\Delta J = +1$ case. If c_2 or $c_3 = 0$ ($c_1 = 1$) in the above expression, the CF term vanishes as expected for the orbitally nondegenerate ${}^6S_{5/2}$ state. And, if it is assumed that the g factors for the ${}^6S_{5/2}$ and ${}^4P_{5/2}$ states are equal (from the Lande equation they are 2.0 and 1.6 respectively), x becomes $g\mu_B/kT$. The coefficient c_3 is expected to be small and hence the last term is dropped from the above expression for x .

Evaluation of Mixing Coefficients

To evaluate c_1 and c_2 which occur in Eq. (28) and (29) the following interstate SO matrix must be evaluated

$$\begin{bmatrix} \langle {}^4P_{5/2} | H_{SO} | {}^4P_{5/2} \rangle + \Delta E & \langle {}^4P_{5/2} | H_{SO} | {}^6S_{5/2} \rangle \\ \langle {}^6S_{5/2} | H_{SO} | {}^4P_{5/2} \rangle & \langle {}^6S_{5/2} | H_{SO} | {}^6S_{5/2} \rangle \end{bmatrix} \quad (30)$$

where ΔE is the energy difference between the two states before SO mixing. The energy of the ${}^6S_{5/2}$ state is taken to be zero.

Both the ${}^6S_{5/2}$ and ${}^4P_{5/2}$ states have $\dots 5d^5 6s^2$ electronic configurations. The 6s electrons will not contribute to any SO coupling; however, the 5d ones will. The SO matrix elements of an l^n electron configuration may be found⁶² using

$$\langle 1^n_{\alpha L S J M_J} | H_{SO} | 1^n_{\alpha' L' S' J' M_J'} \rangle = (-1)^{L+S'+J} \langle \zeta \rangle_{nl} \delta_{JJ'} \delta_{M_J M_J'} \quad (31)$$

$$\times [(2L+1)(1+1)1]^{1/2} \begin{Bmatrix} L & S & J \\ S' & L' & 1 \end{Bmatrix} \langle 1^n_{\alpha L S} || V^{(11)} || 1^n_{\alpha' L' S'} \rangle$$

Inserting tabulated values for the 6j coefficients⁶¹ and reduced matrix elements⁶² ($V^{(11)}$) leads to the secular determinant

$$\begin{vmatrix} E - \epsilon & -\sqrt{5} \langle \zeta \rangle_{5d} \\ -\sqrt{5} \langle \zeta \rangle_{5d} & -\epsilon \end{vmatrix} = 0 \quad (32)$$

Evaluating the characteristic polynomial with $\langle \zeta \rangle_{5d} = 2229 \text{ cm}^{-1}$ for the $4P_{5/2}$ state³⁵ and setting the eigenvalue difference $\Delta\epsilon$ equal to the gas phase energy separation of 11584 cm^{-1} , the energy separation before SO interaction (ΔE) is found to be 5901 cm^{-1} . Thus, $\epsilon_{1,2} = -356.5, 11227.5 \text{ cm}^{-1}$ and $c_1^2 = 0.75$ and $c_2^2 = 0.25$. In other words, we estimate that the $4P_{5/2}$ state is approximately 25% SO mixed into $6S_{5/2}$. Obviously other higher energy states could also be mixed in, but these are ignored here in the present simple treatment.

MCD Moments for Overlapped Multiplets

The above expression (33) for MCD saturation are applicable only for isolated, nonoverlapped bands. For overlapped bands, a different approach must be used. Such a case might arise if the SO splitting in a particular electronic state is not sufficiently large to separate and resolve transitions to its different multiplets. The approach chosen then is to plot the reduced first moment versus inverse temperature. The appropriate expression for P $\leftarrow$ S transitions of any multiplicity has been given⁶³ previously

$$\langle \Delta A_1 \rangle / \langle A \rangle_0 = 2(g_{\text{orb}} - a_s \lambda / kT) \mu_B B \quad (33)$$

where g_{orb} is the excited P state g factor, λ is the excited state SO splitting parameter, μ_B is the Bohr magneton and B the magnetic induction. This expression is unaffected by any Jahn-Teller activity in the excited state.³⁷ The quantity a_s above is defined by

$$a_s = -(kT / \mu_B B) \langle S_z \rangle \quad (34)$$

in which $\langle S_z \rangle$ is the thermal average of the ground state spin operator S_z .

For the present system we redefine a_s to account for the orbital angular momentum mixed into the ground state. Now

$$a_s = -\langle kT/\mu_B B \rangle \langle J_z \rangle \quad (35)$$

and expanding we obtain

$$a_s = -(kT/\mu_B B) \sum_{\sigma} \langle G\sigma | J_z | G\sigma \rangle \exp(-\langle G\sigma | H | G\sigma \rangle / kT) / Z \quad (36)$$

where all terms have been defined above, except the partition function Z which is

$$Z = \sum_{\sigma} \exp(-\langle G\sigma | H | G\sigma \rangle / kT) \quad (37)$$

Evaluating the matrix elements in (36) leads to

$$a_s = (kT/Z\mu_B B) [(5/3) \exp(2A/kT) \sinh(5x/6) + \exp(-A/kT) ((11/3) \sinh(11x/6) + \sinh(x/2))] \quad (38)$$

where $x = g\mu_B B/kT$ and g is the "average" g ($=1.8$) value for the $^6S_{5/2}$ and $^4P_{5/2}$ states. Expression (38) is similar to Eq. (28) given above. A reduced first moment plot vs. inverse temperature as indicated by expression (33) is not expected to yield a straight line because of the temperature dependence in the new a_s given in

Eq. (38). For zero CF splitting in an orbitally nondegenerate state, a_s was found earlier⁶³ to be equal to $2S(S + 1)/3$, i.e. temperature independent.

Results

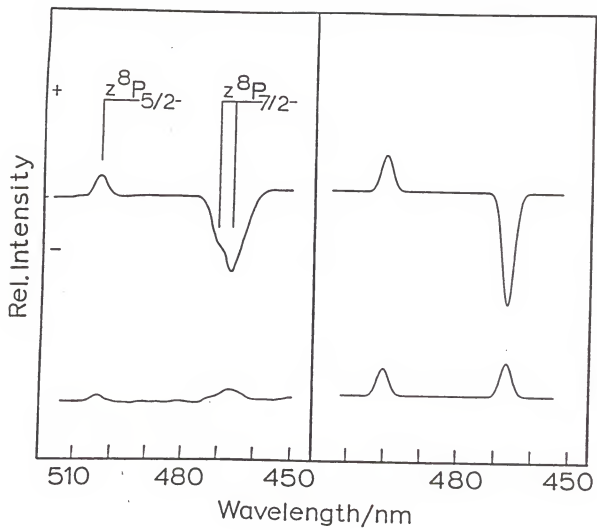
Spectral Assignments

The absorption and MCD spectra of Re isolated in solid Kr are shown in Fig. 7. For each of the three regions simulated spectra are also given. The simulated absorption spectra have been calculated from the relative positions and intensities (gf values) of the gas phase bands (cf. Table 12). Gaussian band shapes have been assumed and the band widths (constant for all bands in absorption and MCD within a given region) chosen to match the observed spectra. The spectra have been shifted from gas phase positions to match the matrix ones (cf. Table 12 for shifts). The simulated MCD band strengths and signs were calculated from the gas phase intensity values multiplied by the predicted C_0/D_0 values. The latter are^{64,65} : g_a for $\Delta J = 0$ transitions, $-Jg_a$ for $\Delta J = +1$ transitions and $(J + 1)g_a$ for $\Delta J = -1$ transitions.

Figure 7

Absorption and MCD Spectra of Re in a Kr Matrix at 10 K

- a) 510-450 nm Region: Left Panel, Observed MCD (Top) and Absorption (Bottom). Right Panel Simulated Spectra.
- b) 360-270 nm Region: Left Panel, Observed MCD (Top) and Absorption (Bottom). Right Panel Simulated Spectra.
- c) 280-220 nm Region: Observed Spectra.
- d) 280-220 nm Region: Simulated Spectra.



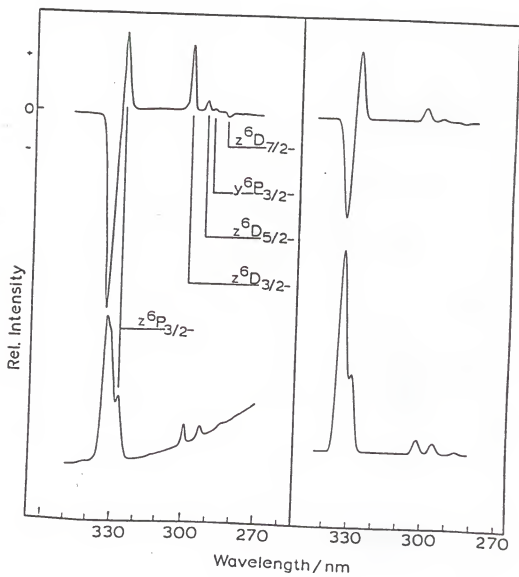


Figure 7--continued

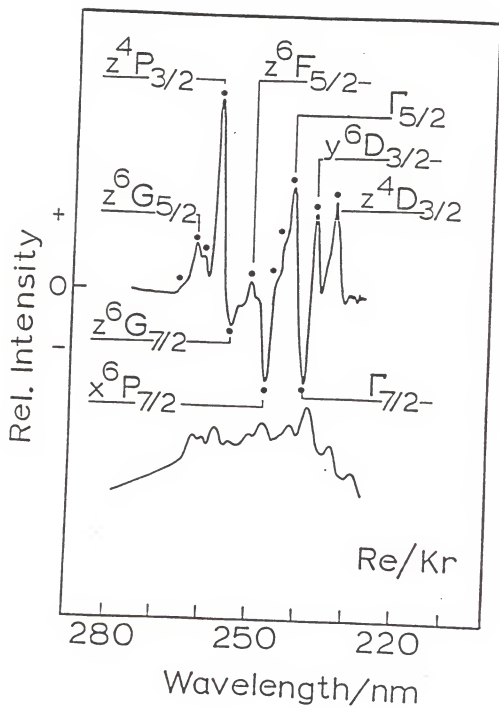


Figure 7--continued

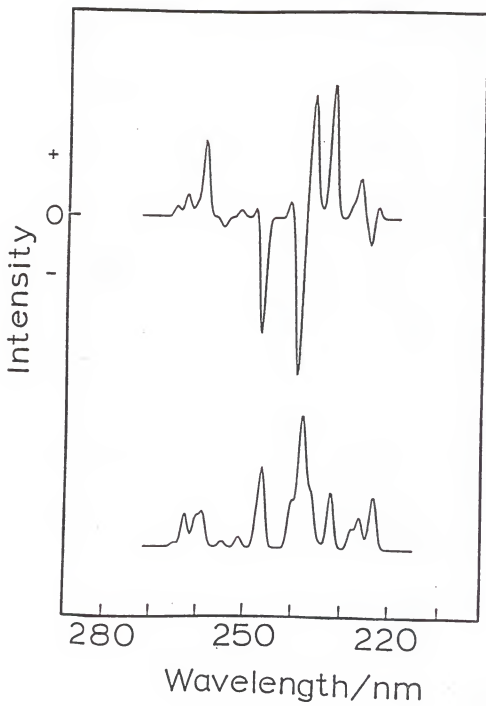


Figure 7--continued

Table 12

Positions, Assignments, and Matrix Shifts of MCD Bands of Re Atoms Isolated in a Krypton Matrix (12 K).

Assignment	$\lambda(\text{nm})$	$\bar{\nu}_{\text{vac}}(\text{cm}^{-1})$	MCD Sign	$\bar{\nu}_{\text{gas}}(\text{cm}^{-1})^{\text{a}}$	$\Delta\bar{\nu}(\text{cm}^{-1})^{\text{b}}$	100gf
$z^8\text{P}_{5/2}$	504.0	19836	+	18950	886	0.76
$z^8\text{P}_{7/2}$	470.0	21271	-	20448	823	1.31
$z^8\text{P}_{7/2}$	466.5	21431	-	20448	983	1.31
$z^6\text{P}_{5/2}$	332.8	30040	-	28854	1186	88
$z^6\text{P}_{7/2}$	331.2	30185	-	28890	1295	120
$z^6\text{P}_{3/2}$	327.5	30526	+	28962	1564	36
$z^6\text{D}_{3/2}$	299.8	33346	+	32592	754	7
$z^6\text{D}_{5/2}$	293.1	34109	+	33409	700	8.2
$y^6\text{P}_{3/2}$	290.0	34473	+	33589	884	1.5
$z^6\text{D}_{7/2}$	284.0	35201	-	34520	681	2.8
$z^6\text{G}_{3/2}$	265.0	37725	+	37064	661	0.84
$z^6\text{G}_{5/2}$	262.2	38128	+	37381	747	9.6
$\Gamma_{5/2}$	260.5	38376	+	37698	678	7.2
$z^6\text{F}_{7/2}$				37766		1.7
$z^4\text{P}_{3/2}$	257.3	38854	+	37916	938	6.3
$z^6\text{G}_{7/2}$	254.5	39281	-	38521	760	2.3
$z^6\text{F}_{5/2}$	250.4	39924	+	39065	859	3.2
$\Gamma_{5/2}$				39671		8.3
$x^6\text{P}_{7/2}$	247.0	40474	-	39845	629	28
$z^6\text{F}_{3/2}$	244.5	40887	+	39927	960	NG ^d

Table 12--continued

Assignment	$\lambda(\text{nm})$	$\bar{\nu}_{\text{vac}}(\text{cm}^{-1})$	$\overset{\text{MCD}}{\text{Sign}}$	$\bar{\nu}_{\text{gas}}(\text{cm}^{-1})^{\text{a}}$	$\Delta\bar{\nu}(\text{cm}^{-1})^{\text{b}}$	100gf
$\Gamma_{3/2}$	243.3	41089	+	40809	280	NG
$\Gamma_{5/2}$	241.5	41395	+	40822	573	11
$Y^6D_{7/2}$				40947		5.9
$\Gamma_{7/2}$	238.7	41881	-	41164	717	39
$Y^6D_{5/2}$				41313		18
$Y^6D_{3/2}$	238.0	42004	+	41557	447	9.6
$\Gamma_{7/2}$				41844		2.0
$z^4D_{3/2}$	233.0	42905	+	42254	651	11
$z^4D_{5/2}$				43044		5.5
$\Gamma_{3/2}$				43342		4.3
$z^4D_{7/2}$				43408		3.9
$\Gamma_{7/2}$				43815		8.6
$\Gamma_{5/2}$				43950		11
$\Gamma_{5/2}$				44054		NG

^a Ref. 35.

^b $\Delta\bar{\nu} = \bar{\nu}_{\text{vac}} - \bar{\nu}_{\text{gas}}$; $\bar{\nu}_{\text{vac}}$ is the matrix value corrected for the refractive index of air.

^c C.H.Corliss and W.R.Bozman, Natl.Bur.Stan.Monograph 53, 1962.

^d none given

Here, g_a is the ground state g value. It can be seen that the observed and simulated spectra in the two lower regions are in close accord. Some minor differences are discussed below. The simulated spectra in the 220-280 nm range are distorted in the 243-241 nm region since there are no available gas phase intensity values for the $z^6F_{3/2}$ and $\Gamma_{3/2}$ bands occurring there. Nevertheless, the appearance of the negative MCD peaks in the simulations enables their assignment in the observed spectrum to $J = 7/2$ multiplets.

In Table 12 are given the observed band positions, assignments, observed MCD C term signs, and matrix shifts. The assignments of the bands were guided from the vapor phase studies¹ and the predicted signs of the MCD C terms.⁶³ Transitions from a $J = 5/2$ multiplet to $J = 3/2$ and $5/2$ multiplets are predicted to have positive C terms while those to $J = 7/2$ multiplets are expected to have negative C terms.⁶³ Although this expectation is usually met in practice, there is one situation seen to date where it is not. For those transitions from an S ground state to a P excited state of the same multiplicity in which an electron is promoted from an s to an p orbital, the $\Delta J = 0$ transition has been found to give a negative C term.^{64,65} A positive one is predicted. This is known³² to develop because of the vibronic mixing of the excited state components via the Jahn-Teller (JT) effect.

In the present system this is observed in the $6P$ system at ≈ 330 nm. The order in the gas phase is $6P_{5/2}$, $6P_{7/2}$, $6P_{3/2}$ (with increasing energy)³⁵ so the predicted C term signs (in the absence of the JT effect) should be positive, negative, positive, respectively. The observed signs are negative, negative (unresolved) and positive. There is other evidence for JT activity in this band system. There appears to be JT activity also in the lower energy $8P$ band system in the 510-450 nm region. The first band at 504.0 nm is assigned to the $z^8P_{5/2}$ multiplet. It exhibits a positive C term, as expected. Two bands are observed at 470.0 and 466.5 nm (seen clearly only in MCD) when only one band (the $z^8P_{7/2}$) is expected. Both show negative C terms, as predicted for a $J = 7/2$ multiplet. The appearance of two negative bands in the matrix MCD is, we believe, attributable to the lifting of the multiplet degeneracy as a result of JT activity. Further analysis would be necessary to prove this contention.

Jahn-Teller Activity

To test whether the $6P_J \leftarrow 6S_{5/2}$ transition (330 nm) is undergoing Jahn-Teller activity due to nontotally symmetric vibrations of the matrix cage, use was made of the following reduced moment equations⁶³

$$\begin{aligned} \langle \Delta A \rangle_3 / \langle A \rangle_0 &= -6a_s \lambda ([\langle E^2 \rangle_C + \langle E^2 \rangle_{NC}/2] \\ &+ a_s \lambda^2/2) \mu_B B / kT \end{aligned} \quad (39)$$

and

$$\langle A \rangle_2 / \langle A \rangle_0 = \langle E^2 \rangle_C + \langle E^2 \rangle_{NC} + a_s \lambda^2 \quad (40)$$

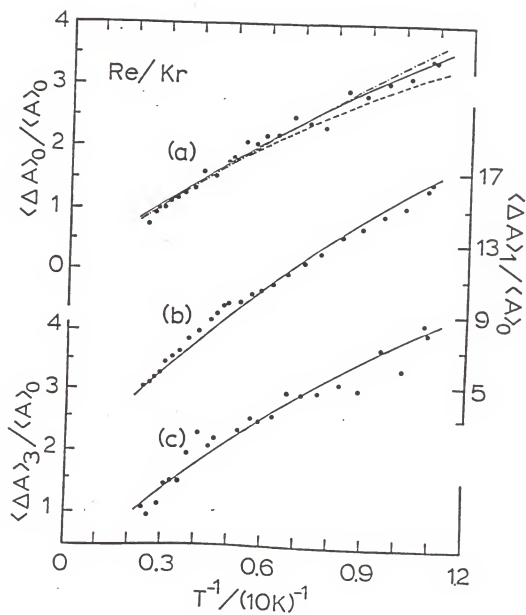
where $\langle E^2 \rangle_C$ and $\langle E^2 \rangle_{NC}$ are the bandwidth contributions from lattice modes of cubic (a_{1g}) and noncubic (e_g and t_{2g}) symmetry, respectively. The SO constant (λ) in these expressions was taken from the fitting of the reduced first moment plot and the A parameter in the a_s Eq.(38) from the reduced zeroth moment plot (vide infra).

In Fig. 8(c) is shown the $\langle \Delta A \rangle_3 / \langle A \rangle_0$ vs $1/T$ plot. The quantity in square brackets in Eq. (39) was varied to obtain the fit shown by the solid line. The best fit result was $\langle E^2 \rangle_C + \langle E^2 \rangle_{NC}/2 = 5.48 \times 10^4 \text{ cm}^{-1}$. Values of $\langle A \rangle_2 / \langle A \rangle_0$ over the same temperature range were independent of temperature. From Eq.(40) the quantity $\langle E^2 \rangle_C + \langle E^2 \rangle_{NC}$ was found to be $6.11 \times 10^4 \text{ cm}^{-1}$. Solving these two equations we find that $\langle E^2 \rangle_C = 4.86 \times 10^4 \text{ cm}^{-1}$ and $\langle E^2 \rangle_{NC} = 1.25 \times 10^4 \text{ cm}^{-1}$. Thus we conclude that the JT effect is operational in this band system although the cubic mode activity is more important.

Figure 8

Reduced Moment Plots vs. Inverse Temperature

- a) Zeroth Moment Plot for the $z^6D_{3/2}$ Band.
For Solid Line Fit $A = 1.5\text{cm}^{-1}$; For
Dash-Dot Line $A = 1.5\text{cm}^{-1}$, and for
Dashed Line $A = 3.5\text{cm}^{-1}$. Use Upper Left
Hand Ordinate.
- b) Reduced First Moment Plot for the z^6P_J
Band. Use Middle Right Hand Ordinate.
- c) Reduced Third Moment Plot for the z^6P_J
Band. Use Lower Left Hand Ordinate.
Ordinate Should be Multiplied by 1.8×10^6 .



MCD Saturation Results

The approach taken here has been to measure the temperature dependence (at fixed magnetic field strength) of several optical MCD/absorption bands of Re/Kr, and then fit these results to the appropriate theoretical expression (cf. Eqs. (28) and (33)). In doing so the ground state crystal field splitting and excited state (z^6P) spin-orbit coupling constant were extracted. For the technique to provide reliable data, it is usually necessary to choose for study bands which are reasonably strong and not overlapped with other bands. The $z^6D_{3/2}$ band at 299.8 nm is an excellent candidate. The $z^8P_{5/2}$ band at 504.0 nm and the $z^8P_{7/2}$ band at 470.0/466.5 nm were also attempted, but the results were unsatisfactory (high scatter), presumably due to weak absorption. Finally the ^6P band system at approximately 330 nm was also chosen although it does not fit the no overlap criterion.

Rather than plot peak heights, we choose instead to use a moment of the entire band or group of bands. The moments are defined⁶⁰ as

$$\langle A \rangle_n = \int (A/\epsilon)(\epsilon - \bar{\epsilon})^n d\epsilon \quad (41)$$

$$\langle \Delta A \rangle_n = \int (\Delta A/\epsilon)(\epsilon - \bar{\epsilon})^n d\epsilon \quad (42)$$

where $\langle A \rangle_n$ and $\langle \Delta A \rangle_n$ are the n th absorption and MCD moments, respectively, and $\bar{\epsilon}$ is the average band energy defined so that $\langle A \rangle_1 = 0$. Also, $A = (A_+ + A_-)/2$ and $\Delta A = A_- - A_+$ where A_+ (A_-) is the absorbance of right (left) circularly polarized light. Reduced moment plots are preferred since they are concentration independent whereas the MCD or absorption moments alone are not. Any potential problems due to loss of sample and/or matrix material during any of the temperature runs are thereby avoided.

For the ${}^6D_{3/2}$ band (≈ 3000 nm) a reduced zeroth moment ($\langle \Delta A \rangle_0 / \langle A \rangle_0$) plot was made and is shown in Fig.8(a). For a ground state which exhibits no crystal field splitting and normal Zeeman splitting such a plot is usually linear with the magnetic field (0.5 T) and the temperature range (9.2-42 K) used here. Clearly the present plot is nonlinear, indicating a substantial ground state splitting. It is also apparent from the figure that saturation (zero slope) has not yet been reached at the lowest temperatures employed here. The plot in Fig.8(a) was fit to saturation expression (28) using a least squares fitting procedure and varying the splitting parameter A . The solid line is the best fit ($A = 2.5 \text{ cm}^{-1}$). To give an indication of the sensitivity of the fit to A , we have also plotted the curves for $A = 1.5$ and 3.5 cm^{-1} . The actual crystal field splitting is thus found to be $3 \times (2.5 \pm 1.0) \text{ cm}^{-1} = 7.5 \pm 3.0 \text{ cm}^{-1}$.

The approach used for the ${}^6P$ band (≈ 330 nm) is different. Because the three J multiplets ($3/2, 7/2, 5/2$) are severely overlapped, we used the approach outlined earlier.

The reduced first moment ($\langle \Delta A \rangle_1 / \langle A \rangle_0$) was plotted versus $1/T$ in Fig.8(b). Expression (33) with a_s as defined in Eq.(38) was fit to this plot. Since x in Eq. (38) is small, the hyperbolic sine term can be expanded as $\sinh(y) \approx y$ which leads to

$$a_s \approx (25g/18Z)\exp(2A/kT) + (65g/9Z)\exp(-A/kT) \quad (43)$$

The CF splitting factor A was taken from the previous fit to the ${}^6D_{3/2}$ band and the parameter λ varied until the fit shown in the figure obtained. As can be seen the fit is excellent and leads to a SO splitting parameter, $\lambda = -102 \text{ cm}^{-1}$. Comparison of this value to the gas phase value is difficult since the multiplet order is perturbed, i.e. $5/2 < 7/2 < 3/2$ (energetically) and the Lande interval rule not simply applicable.

Discussion

The question has been addressed as to why rhenium trapped in a low temperature matrix does not give an ESR spectrum even though its ground state is ${}^6S_{5/2}$. By using the MCD saturation method with an appropriate theoretical model, we have shown that the ${}^6S_{5/2}$ state is spin-orbit coupled with a low lying ${}^4P_{5/2}$ excited state, and that in a tetradecahedral substitutional matrix site, this mixed state is split by crystal field forces. The splitting between the U' and E'' components is found to be 7.5 cm^{-1} .

ESR transitions between the α'' and β'' Zeeman split components of E'' are expected to be largely forbidden since the major $|J M_J\rangle$ components of these states are $|5/2 -3/2\rangle$ and $|5/2 3/2\rangle$, respectively. At low temperatures it is expected that no ESR signal should be observable between these components. The transition between an E'' component and a U' component is also not expected since the splitting ($7.5 \text{ cm}^{-1} = 225 \times 10^9 \text{ Hz}$) is approximately 24 times larger than the normal X-band ESR resonance frequency ($9.3 \times 10^9 \text{ Hz}$)⁴⁸. Transitions between the $|U'\lambda\rangle$ and $|U'\mu\rangle$ components ($|5/2 1/2\rangle$ and $|5/2 -1/2\rangle$) are, however, predicted to be observable at elevated temperatures (25-30 K).

This study reinforces the idea that rare gas matrices have a significant influence on the species isolated in them. Recent studies have shown that matrices influence the magnitude and sign of the spin-orbit coupling of metal excited P states, induce vibronic mixing of excited state multiplets, enhance spin forbidden transitions, and, as shown here, are responsible for large ground state splittings.

CHAPTER 4 ATOMIC MCD AND MLD SATURATION THEORY

MCD Saturation Theory

The magnetic circular dichroism (MCD) saturation technique, which involves the monitoring of an MCD peak intensity as a function of temperature and/or magnetic field strength, has been used in a number of cases to probe the nature (g value) of various matrix isolated atoms and molecules.⁶⁶⁻⁶⁸ In certain cases this method is preferred over the moment analysis procedure which involves the computation of the ratio C/D where C is a Faraday parameter associated with a degenerate ground state and D is the dipole strength. This latter method frequently suffers as a result of large experimental errors due to uncertainty in the baseline and also from diamagnetic impurities which affect the determination of D. The saturation method bypasses these two pitfalls.

In this section, general expressions for the MCD, $\Delta A (= A_L - A_R$ where A_L (A_R) is the absorbance of left (right) circularly polarized light) are derived for the case where the ground state is split by a crystal (matrix) field.

Our starting point is the expression^{60,69}

$$\Delta A = (\sigma \epsilon f c y / Z) \sum_{\alpha} \sum_{\beta} \exp(-\langle A\alpha | H | A\alpha \rangle / kT) \times \\ [| \langle A\alpha | m_a | B\beta \rangle |^2 - | \langle A\alpha | m_b | B\beta \rangle |^2] \quad (44)$$

where $\sigma = 2N_0 n^3 \log_{10} e / 250hc'$, ϵ is the photon energy, Z is the electronic partition function, f the bandshape function, c the concentration, y the pathlength, A the electronic ground state (component α) and B is the excited state (component β). The total Hamiltonian, H is given by $H = H_Z + H_{CF}$ where H_{CF} is the crystal field Hamiltonian and $H_Z (= g\mu_B B J_Z)$ is the Zeeman operator. The transition moment operators are $m_a = m_- = (m_x - im_y)/\sqrt{2}$ and $m_b = m_+ = (m_x + im_y)/\sqrt{2}$ for MCD where m_x and m_y are the cartesian components of the space fixed electric dipole operator.

In the presence of a crystal field, we can expand the atomic ground state wavefunctions in a $|JM\rangle$ basis as follows

$$|A\alpha\rangle = \sum_M \sum_{J'M} \frac{A\alpha}{J'M} |J'M\rangle \quad (45)$$

where the expansion coefficients are tabulated in Butler⁷⁰ for various crystal symmetries.

Inserting Eq.(45) into Eq.(44), defining $\langle A\alpha | H | A\alpha \rangle \equiv E_{\alpha}$, and using $|B\beta\rangle = |J\beta\rangle$ (spectroscopic stability applies to the excited state basis.) we obtain

$$\Delta A_{\text{MCD}} = (\sigma e f c y / Z) \sum_{\alpha} \sum_{\beta} \exp(-E_{\alpha}/kT) [\sum_M^{A\alpha} c_{J',M} \langle J'M | m_- | J\beta \rangle^2 - \sum_M^{A\alpha} c_{J',M} \langle J'M | m_+ | J\beta \rangle^2] \quad (46)$$

Application of the Wigner-Eckart theorem and the properties of the 3j symbol we find

$$\Delta A_{\text{MCD}} = (\sigma e f c y / Z) | \langle J' || m || J \rangle |^2 \sum_{\alpha} \sum_{\beta} \exp(-E_{\alpha}/kT) \times \quad (47)$$

$$[|c_{J',\beta-1}|^2 \begin{pmatrix} J' & 1 & J \\ 1-\beta & -1 & \beta \end{pmatrix}^2 - |c_{J',\beta+1}|^2 \begin{pmatrix} J' & 1 & J \\ -\beta-1 & 1 & \beta \end{pmatrix}^2]$$

where $\langle J' || m || J \rangle$ is the reduced matrix element. The 3j symbols can be evaluated analytically⁷¹; the pertinent expressions for the electric dipole allowed transitions $\Delta J = \pm 1, 0$ are given in Table 13.

We now proceed with the case $\Delta J = -1$ ($J' \rightarrow J'-1$). Inserting the appropriate expressions from Table 13 we get

Table 13
 $(3j)^2$ for Electric Dipole Transitions

$\Delta J = +1$

$$\begin{pmatrix} J' & 1 & J'+1 \\ 1-\beta & -1 & \beta \end{pmatrix}^2 \quad \frac{(J'+\beta)(J'+\beta+1)}{2(2J'+1)(J'+1)(2J'+3)}$$

$$\begin{pmatrix} J' & 1 & J'+1 \\ -\beta & -1 & \beta \end{pmatrix}^2 \quad \frac{(J'-\beta)(J'-\beta+1)}{2(2J'+1)(J'+1)(2J'+3)}$$

$$\begin{pmatrix} J' & 1 & J'+1 \\ -\beta & 0 & \beta \end{pmatrix}^2 \quad \frac{2(J'+\beta+1)(J'-\beta+1)}{2(2J'+1)(J'+1)(2J'+3)}$$

$\Delta J = 0$

$$\begin{pmatrix} J' & 1 & J' \\ 1-\beta & -1 & \beta \end{pmatrix}^2 \quad \frac{(J'-\beta+1)(J'+\beta)}{2J'(J'+1)(2J'+1)}$$

$$\begin{pmatrix} J' & 1 & J' \\ -\beta-1 & 1 & \beta \end{pmatrix}^2 \quad \frac{(J'+\beta+1)(J'-\beta)}{2J'(J'+1)(2J'+1)}$$

$$\begin{pmatrix} J' & 1 & J' \\ -\beta & 0 & \beta \end{pmatrix}^2 \quad \frac{2\beta^2}{2J'(J'+1)(2J'+1)}$$

$\Delta J = -1$

$$\begin{pmatrix} J' & 1 & J'-1 \\ 1-\beta & -1 & \beta \end{pmatrix}^2 \quad \frac{(J'-\beta)(J'-\beta+1)}{2(2J'-1)J'(2J'+1)}$$

$$\begin{pmatrix} J' & 1 & J'-1 \\ -\beta-1 & 1 & \beta \end{pmatrix}^2 \quad \frac{(J'+\beta)(J'+\beta+1)}{2J'(2J'-1)(2J'+1)}$$

$$\begin{pmatrix} J' & 1 & J'-1 \\ -\beta & 0 & \beta \end{pmatrix}^2 \quad \frac{2(J'-\beta)(J'+\beta)}{2J'(2J'-1)(2J'+1)}$$

$$\Delta A_{\text{MCD}}^{(-1)} = \frac{(\sigma \epsilon f c y |\langle J' || m || J'-1 \rangle|^2}{2Z(2J'-1)J'(2J'+1)} \sum_{\alpha} \sum_{\beta} \exp(-E_{\alpha}/kT) \times \quad (48)$$

$$[|c_{J', \beta-1}^{A\alpha}|^2 (J'-\beta)(J'-\beta+1) - |c_{J', \beta+1}^{A\alpha}|^2 (J'+\beta)(J'+\beta+1)]$$

To simplify this, the term in brackets is written out explicitly for the ground state crystal field components 1 (let $\beta = \beta_1$) and 2 (let $\beta = -\beta_1$)

$$|c_{J', \beta_1-1}^{(1)}|^2 (J'-\beta_1)(J'-\beta_1+1) - |c_{J', \beta_1+1}^{(1)}|^2 (J'+\beta_1)(J'+\beta_1+1) \quad (49)$$

$$|c_{J', -\beta_1-1}^{(2)}|^2 (J'+\beta_1)(J'+\beta_1+1) - |c_{J', -\beta_1+1}^{(2)}|^2 (J'-\beta_1)(J'-\beta_1+1) \quad (55)$$

At this point it is crucial to understand the qualitative behavior of the atomic eigenstates in the presence of both an external crystalline electric field as well as a magnetic field. If we evaluate the Zeeman energies $\langle A\alpha | H_Z | A\alpha \rangle$ using Eq.(45) we find

$$\langle A\alpha | H_Z | A\alpha \rangle = g\mu_B B \sum_M |c_{J', M}^{A\alpha}|^2 M \quad (51)$$

Here we have ignored any off diagonal Zeeman coupling terms between the crystal field states. For relatively small magnetic fields, this approximation should not adversely affect our results. In Table 14, we present the results of a full diagonalization of the Zeeman-crystal field matrix for the case of Fe ($^5D_4$ ground state) isolated in a tetragonal Xe matrix site (crystal field parameters $F = 0.66 \text{ cm}^{-1}$ and $B = 0.49 \text{ cm}^{-1}$; $g = 1.5$). In a tetragonal field the $J = 4$ gas phase ground state is split into A_1 , T_1 , T_2 , and E crystal components⁵⁹ some of which are mixed by the magnetic field. For example, the $|T_1+1\rangle$ and $|T_2-1\rangle$ components (zero field splitting = 11.9 cm^{-1}) mix to give two orthonormal eigenstates of the form

$$\phi = c_1 |T_1+1\rangle + c_2 |T_2-1\rangle \quad (52)$$

It is these coefficients that we tabulate in Table 14. As can be seen, the magnetic mixing is small and hence the crystal field states $|A_a\rangle$ are an excellent approximation to the true eigenstates. An exception to this involves the case where the zero magnetic field crystal states happen to be degenerate or nearly degenerate. In this situation the off diagonal Zeeman matrix elements are critical.

Table 14

Crystal Field Mixing Coefficients as a Function
of Magnetic Field Strength

B (Tesla)	C_1	C_2
0.21	0.9999	-.01575
0.43	0.9995	-.03105
0.64	0.9990	-.04461
0.86	0.9983	-.05781
1.28	0.9968	-.0805
1.93	0.9939	-.1100
2.57	0.9910	-.1339
5.35	0.9796	-.2001

Application of the time reversal operator⁷⁰, K_t , to $|A\alpha\rangle$ yields

$$K_t |A\alpha\rangle = k_{A\alpha} |A\alpha'\rangle = \sum_M (c_{J'M}^{A\alpha})^* (-1)^{J'-M} |J'-M\rangle \quad (53)$$

where $k_{A\alpha}$ is a phase of modulus one, and $|A\alpha'\rangle$ is the Kramer's conjugate of $|A\alpha\rangle$. Therefore,

$$|A\alpha'\rangle = \sum_M (c_{J'M}^{A\alpha})^* k_{A\alpha}^* (-1)^{J'-M} |J'-M\rangle \quad (54)$$

As a result, the contribution, $|c_{J'M}^{A\alpha}|^2$, of $|J'M\rangle$ to $|A\alpha\rangle$ is equal to the contribution, $|(c_{J'M}^{A\alpha})^* k_{A\alpha}^* (-1)^{J'-M}|^2$, of $|J'-M\rangle$ to $|A\alpha'\rangle$. From this it follows that

$$\langle A\alpha' | H_Z | A\alpha' \rangle = - \langle A\alpha | H_Z | A\alpha \rangle \quad (55)$$

Hence even fold degenerate crystal field states are symmetrically split about a barycenter. Oddly degenerate states possess at least one self conjugate component for which Eq.(51) yields zero (i.e. no first order magnetic effect). In certain cases such as the $|E\theta\rangle$ and $|E\epsilon\rangle$ crystal components (O_h) of $J = 4$, both states are unaffected by a magnetic field.

This behavior is illustrated in Fig.9 for a hypothetical $J = 4$ manifold (9 fold degenerate) crystal field split into one 2, one 3, and one 4 fold degenerate crystal field state (arbitrary energetic ordering).

If we allow components 1 and 2 in Eqs.(49) and (50) to represent Kramer's conjugate states and use the time reversal results

$$|c_{J', \beta_1-1}^{(1)}|^2 = |c_{J', -\beta_1+1}^{(2)}|^2 \quad (56)$$

$$|c_{J', \beta_1+1}^{(1)}|^2 = |c_{J', -\beta_1-1}^{(2)}|^2$$

we find that Eq.(48) becomes

$$\Delta A_{MCD}^{(-1)} = \frac{-g\epsilon fcy |\langle J' || m || J'-1 \rangle|^2}{2ZJ'(2J'-1)(2J'+1)} \sum_i \sum_j \sum_\beta \exp(-E_{CF_i}/kT) \times$$

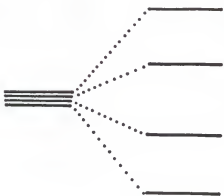
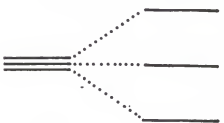
$$2\sinh(E_{Z(i,j)}/kT) \times \quad (57)$$

$$[|c_{J', \beta-1}^{(i,j)}|^2 (J'-\beta)(J'-\beta+1) - |c_{J', \beta+1}^{(i,j)}|^2 (J'+\beta)(J'+\beta+1)]$$

Figure 9

Behavior of the Free Atom $|JM\rangle$ States in the
Presence of a Crystal and Magnetic Field.

$$\begin{aligned} \text{a) } H_{CF} &\neq 0, H_Z = 0 \\ \text{b) } H_{CF} &\neq 0, H_Z \neq 0 \end{aligned}$$

E_3  E_3 E_2  $E_2 + c_3 \gamma$ $E_2 + c_2 \gamma$ $E_2 - c_2 \gamma$ $E_2 - c_3 \gamma$ E_1 

a

b

 $E_1 + c_1 \gamma$ E_1 $E_1 - c_1 \gamma$

where the sum over α has been split into a sum over crystal field states, i , and a sum over the positive energy (Zeeman) Kramer's components, j . The energies E_α have been rewritten as (See Fig.9)

$$E_\alpha = E_{CF_i} + E_{Z(i,j)} \quad (58)$$

with the Zeeman energies given by

$$\begin{aligned} E_{Z(i,j)} &= g\mu_B B \left| c_{J',M}^{(i,j)} \right|^2_M \\ &\equiv g\mu_B B \langle M \rangle^{(i,j)} \end{aligned} \quad (59)$$

Finally, each pair of Kramer's conjugate state energies has been collected as a hyperbolic sine function.

To simplify the term in brackets, we let $\beta = M+1$ in the first term and $\beta = M-1$ in the second term. Note $M \neq \pm J'$, $\pm(J'-1)$ because $\beta = M+1$ does not exist for $M = J'$ or $J'-1$. Recall we are dealing with the case $\Delta J = -1$, i.e. $J' \rightarrow J'-1$ and M is the ground state magnetic quantum number ranging from $-J'$ to $+J'$ and β is the excited state magnetic quantum number ranging from $-(J'-1)$ to $+(J'-1)$. Similarly $\beta = M-1$ does not exist for $M = -J'$ or $-(J'-1)$.

The coefficient of $|c_{J',M}|^2$ is therefore

$$(J'-M-1)(J'-M) - (J'+M-1)(J'+M) = -2M(2J'-1) \quad (60)$$

For the 4 cases $M = \pm J', \pm(J'-1)$ the term in brackets is

$$\begin{aligned} & 2(2J'-1)[J'(|c_{J',-J'}|^2 - |c_{J',J'}|^2) \\ & + (J'-1)(|c_{J',-J'+1}|^2 - |c_{J',J'-1}|^2)] \end{aligned} \quad (61)$$

Substituting Eqs.(60) and (61) into Eq.(57) we obtain

$$\begin{aligned} \Delta A_{MCD}^{(-1)} = & \frac{-\sigma \epsilon f c y |\langle J' || m || J'-1 \rangle|^2}{2(2J'-1)J'(2J'+1)} \sum_i \sum_j \exp(-E_{CF_i}/kT) \times \\ & \sinh(E_{Z(i,j)}/kT) \times \end{aligned} \quad (62)$$

$$\begin{aligned} & -2(2J'-1)[\sum_M |c_{J',M}|^2 + J'(|c_{J',J'}|^2 - |c_{J',-J'}|^2) \\ & + (J'-1)(|c_{J',J'-1}|^2 - |c_{J',-J'+1}|^2)] \end{aligned}$$

The term in brackets however is just $\langle M \rangle^{(i,j)}$. Hence we have

$$\Delta A_{\text{MCD}}^{(-1)} = \frac{2\sigma\epsilon fcy |\langle J' || m || J'-1 \rangle|^2}{2J'(2J'+1)} \sum_i \sum_j \exp(-E_{\text{CF}_i}/kT) x \langle M \rangle^{(i,j)} \sinh(\langle M \rangle^{(i,j)} x) \quad (63)$$

where $x \equiv g\mu_B B/kT$. Therefore it follows that a positive MCD is expected for a $\Delta J = -1$ transition, regardless of the crystal field symmetry.

Proceeding in a similar manner for the $\Delta J = 0, +1$ cases we obtain

$$\Delta A_{\text{MCD}}^{(0)} = \frac{2\sigma\epsilon fcy |\langle J' || m || J'+1 \rangle|^2}{2J'(J'+1)(2J'+1)} \sum_i \sum_j \exp(-E_{\text{CF}_i}/kT) x \langle M \rangle^{(i,j)} \sinh(\langle M \rangle^{(i,j)} x) \quad (64)$$

$$\Delta A_{\text{MCD}}^{(+1)} = \frac{-2\sigma\epsilon fcy |\langle J' || m || J'+1 \rangle|^2}{2(2J'+1)(J'+1)} \sum_i \sum_j \exp(-E_{\text{CF}_i}/kT) x \langle M \rangle^{(i,j)} \sinh(\langle M \rangle^{(i,j)} x) \quad (65)$$

Hence the electric dipole transitions $\Delta J = -1, 0, +1$ are expected to have the signs positive, positive, negative,

respectively, regardless of the nature of the matrix field.

It is interesting to note that for the case of zero crystal field effects, i.e. $|JM\rangle$ eigenstates instead of $|Aa\rangle$, Eqs.(63) - (65) reduce to the form

$$\Delta A_{MCD} \propto \frac{\pm \sum_M M \sinh(Mx)}{Z} \quad (66)$$

since $\langle M \rangle^{(i,j)} \rightarrow M$, $j \rightarrow M$, and the sum over crystal field states, i , as well as $\exp(-E_{CF_i}/kT)$ vanish. Once again, the negative sign holds for the $\Delta J = +1$ case, and the positive sign otherwise.

MLD Saturation Theory

Next, we extend the results of the previous section to include atomic magnetic linear dichroism (MLD). Our starting point again is Eq.(44) with $m_a = m_{\parallel} = m_z$ and $m_b = m_{\perp} = m_x = (m_+ + m_-)/\sqrt{2}$. Inserting Eq.(45) into Eq.(44), using the Wigner-Eckart theorem and the properties of the $3j$ symbols, we obtain

$$\Delta A_{MLD} = \sigma \epsilon f c y \sum_z \langle J' || m || J \rangle^2 \sum_{\alpha} \sum_{\beta} \exp(-E_{\alpha}/kT) [|c_{J',\beta}^{A\alpha}|^2 \begin{pmatrix} J' & 1 & J \\ -\beta & 0 & \beta \end{pmatrix}^2] \quad (67)$$

$$- (1/2) [|c_{J',\beta+1}^{A\alpha}|^2 \begin{pmatrix} J' & 1 & J \\ -\beta-1 & 1 & \beta \end{pmatrix}^2 + |c_{J',\beta-1}^{A\alpha}|^2 \begin{pmatrix} J' & 1 & J \\ -\beta+1 & -1 & \beta \end{pmatrix}^2]]$$

As an illustration of the derivation, we proceed for the $\Delta J = 0$ case with the $\Delta J = \pm 1$ cases being similar. Inserting the appropriate $3j$ expressions from Table 13 we find

$$\begin{aligned} \Delta A_{MLD}^{(0)} &= \frac{\sigma \epsilon f c y \langle J' || m || J \rangle^2}{2Z J'(J'+1)(2J'+1)} \sum_{\alpha} \sum_{\beta} \exp(-E_{\alpha}/kT) [|c_{J',\beta}^{A\alpha}|^2 2\beta^2 \\ &\quad - (1/2) [|c_{J',\beta+1}^{A\alpha}|^2 (J'+\beta+1)(J'-\beta) \\ &\quad + |c_{J',\beta-1}^{A\alpha}|^2 (J'-\beta+1)(J'+\beta)]] \end{aligned} \quad (68)$$

If we rewrite the term in large brackets for ground state crystal components 1 (let $\beta = \beta_1$) and 2 (let $\beta = -\beta_1$) we find analogous to Eqs.(49) and (50)

$$\begin{aligned}
& |c_{J', \beta_1}^{(1)}|^2 2\beta_1^2 - (1/2) [|c_{J', \beta_1 + 1}^{(1)}|^2 (J' + \beta_1 + 1)(J' - \beta_1) \\
& + |c_{J', \beta_1 - 1}^{(1)}|^2 (J' - \beta_1 + 1)(J' + \beta_1)]
\end{aligned} \tag{69}$$

$$\begin{aligned}
& |c_{J', -\beta_1}^{(2)}|^2 2\beta_1^2 - (1/2) [|c_{J', -\beta_1 + 1}^{(2)}|^2 (J' - \beta_1 + 1)(J' + \beta_1) \\
& + |c_{J', -\beta_1 - 1}^{(2)}|^2 (J' + \beta_1 + 1)(J' - \beta_1)]
\end{aligned} \tag{70}$$

Using the time reversal results for the Kramer's conjugate states 1 and 2

$$\begin{aligned}
|c_{J', \beta_1}^{(1)}|^2 &= |c_{J', -\beta_1}^{(2)}|^2 \\
|c_{J', \beta_1 + 1}^{(1)}|^2 &= |c_{J', -\beta_1 - 1}^{(2)}|^2 \\
|c_{J', \beta_1 - 1}^{(1)}|^2 &= |c_{J', -\beta_1 + 1}^{(2)}|^2
\end{aligned} \tag{71}$$

we find that Eqs.(69) and (70) are identical (compare to Eqs.(49) and (50) which differ by a negative sign.) Hence Eq.(68) becomes

$$\Delta A_{\text{MLD}}^{(0)} = \frac{\sigma \epsilon f c y |\langle J' | |m| | J' \rangle|^2}{2ZJ'(J'+1)(2J'+1)} \sum_i \sum_j \sum_{\beta} \exp(-E_{\text{CF}_i} / kT) x$$

$$2 \cosh(\langle M \rangle^{(i,j)} x) x$$

(72)

$$\begin{aligned} & [2 |c_{J', \beta}^{(i,j)}|^2 \beta^2 - (1/2) [|c_{J', \beta+1}^{(i,j)}|^2 (J'+\beta+1)(J'-\beta) \\ & + |c_{J', \beta-1}^{(i,j)}|^2 (J'-\beta+1)(J'+\beta)]] \end{aligned}$$

Note that this expression is only for crystal field components forming Kramer's pairs. It will be modified later to account for non-Kramer's pair states. As before, the sum over α has been broken down into a sum over crystal field states, i , and a sum over the positive energy (Zeeman) Kramer's components.

To simplify the expression in large brackets (3 terms), we let $\beta = M$ in the first term (arising from m_z), $\beta = M-1$ in the second term (arising from m_+), and $\beta = M+1$ in the third term (arising from m_-). Hence the coefficient of $|c_{J', M}|^2$ is

(73)

$$2M^2 - (1/2) [(J'+M)(J'-M+1) + (J'-M)(J'+M+1)] = 3M^2 - J'(J'+1)$$

Note $M \neq \pm J'$ above because $\beta = M+1$ (third term) does not exist for $M = J'$ nor does $\beta = M-1$ (second term) exist for $M = -J'$. Recall that we are dealing with the case $\Delta J = 0$, i.e. $J' \rightarrow J'$. These two cases must be dealt with separately. Hence the term in large brackets gives for these 2 cases

$$(2J'^2 - J') [|c_{J', J'}|^2 + |c_{J', -J'}|^2] \quad (74)$$

It is important to realize that $2J'^2 - J' = 3M^2 - J'(J'+1)$ for $M = J'$. Inserting Eqs.(73) and (74) into Eq.(72) we obtain

$$\begin{aligned} \Delta A_{\text{MLD}}^{(0)} &= \frac{\sigma \epsilon f c y |\langle J' | |m| | J' \rangle|^2}{2J'(J'+1)(2J'+1)} \sum_i \sum_j \exp(-E_{\text{CF}_1}/kT) \times \\ &\quad \cosh(\langle M \rangle^{(i,j)}_x) \times \\ &\quad [[\sum_M (3M^2 - J'(J'+1)) |c_{J', M}^{(i,j)}|^2] + (3J'^2 - J'(J'+1)) \times \\ &\quad [|c_{J', J'}^{(i,j)}|^2 + |c_{J', -J'}^{(i,j)}|^2]] \end{aligned} \quad (75)$$

where the prime over the summation indicates a sum from $M = -J'+1$ to $J'-1$. The term in large brackets is just

$$\begin{aligned} 3 \sum_M^2 |c_{J',M}|^2 - J'(J'+1) \sum |c_{J',M}|^2 \\ \equiv 3 \langle M^2 \rangle^{(i,j)} - J'(J'+1) \end{aligned} \quad (76)$$

where the normalization of the crystal field components has been used in the second term. Therefore,

$$\Delta A_{\text{MLD}}^{(0)} = \frac{\sigma \epsilon f c y |\langle J' || m || J' \rangle|^2}{2 J'(J'+1)(2J'+1)} \sum_i \sum_j \exp(-E_{\text{CF}_i}/kT) \times \quad (77)$$

$$\cosh(\langle M \rangle^{(i,j)} x) [3 \langle M^2 \rangle^{(i,j)} - J'(J'+1)]$$

To take into account non-Kramer's pair states ($\langle M \rangle^{(i,j)} = 0$) we must add a term of the form $(1/2)[3 \langle M^2 \rangle^{(i,*)} - J'(J'+1)]$ for each non Kramer's pair component (note asterisk). Hence our final result is

$$\Delta A_{MLD}^{(0)} = \frac{\sigma \epsilon f c y |\langle J' | m | J' \rangle|^2}{2J'(J'+1)(2J'+1)} \sum_i \exp(-E_{CF_i}/kT) x$$

$$\left[\sum_j [\cosh(\langle M \rangle^{(i,j)} x) [3 \langle M^2 \rangle^{(i,j)} - J'(J'+1)]] \right] \quad (78)$$

$$+ (1/2) [3 \langle M^2 \rangle^{(i,*)} - J'(J'+1)]$$

Proceeding in a similar fashion for the $\Delta J = \pm 1$ cases, we find a equivalent expression to Eq.(78) with the simple changes: For $\Delta J = +1$, replace J' by $-(2J'+3)$ in the denominator and change the second occurrence of J' in the reduced matrix element to $J'+1$. For $\Delta J = -1$, replace $J'+1$ by $-(2J'-1)$ in the denominator and change the second occurrence of J' in the reduced matrix element to $J'-1$. We see therefore that $\Delta J = \pm 1$ transitions are expected to be negative whereas the $\Delta J = 0$ case is expected to yield positive MLD bands.

For the case of zero crystal field splitting, the sum over i as well as $\exp(-E_{CF_i}/kT)$ vanish. In addition, $\langle M^2 \rangle^{(i,j)} = M^2$, and the $\langle M^2 \rangle^{(i,*)}$ term, which is only present in even electron systems (odd degeneracy) equals zero. Therefore,

$$\Delta A_{MLD} \propto \sum_M [\cosh(Mx) [3M^2 - J'(J'+1)]] - J'(J'+1)/2 \quad (79)$$

Recall that the $J'(J'+1)/2$ term is applicable only for integral J' .

Application To Octahedral $J=3$ Ni

As a specific illustration of the formalism developed above, we apply the MCD/MLD saturation technique to the $^3D_3$ state of atomic Ni trapped in a rare gas matrix site of O_h symmetry.⁵⁴ The appropriate basis set to use for an octahedral crystal field with the axis of quantization along the fourfold axis is the octahedral $SO_3-O-D_4-C_4$ set tabulated in Butler.⁷⁰ In Table 15 are presented the basis statevectors in Butler's chain of groups notation as well as the more familiar Mulliken notation. In addition, $\langle M \rangle$ and $\langle M^2 \rangle$ as defined in Eqs. 59 and 76 are given.

Using these results, it is a simple matter to write down (using Eqs. 63 and 78) the MCD and MLD saturation expressions for Ni ($^3D_3$) in an octahedral crystal field.

(80)

$$\Delta A_{MCD}(0) \propto [3\exp(-E_{T_1}/kT)S(3x/2) + \exp(-E_{T_2}/kT)S(x/2)]/Z$$

$$\Delta A_{MLD}(0) \propto [\exp(-E_{T_1}/kT)\{C(3x/2) - 1\}]/Z \quad (81)$$

Table 15
 $\text{SO}_3\text{-O-D}_4\text{-C}_4$ Basis Set Statevectors

	Mulliken <u>Notation</u>	$\langle M \rangle$	$\langle M^2 \rangle$
$ 3\ 1\ 0\ 0\rangle$	T_1	0	0
$ 3\ 1\ 1\ 1\rangle$	T_1	$-3/2$	6
$ 3\ 1\ 1\ -1\rangle$	T_1	$3/2$	6
$ 3\ 1\ 1\ 1\rangle$	T_2	$-1/2$	4
$ 3\ 1\ 1\ -1\rangle$	T_2	$1/2$	4
$ 3\ 1\ 2\ 2\rangle$	T_2	0	4
$ 3\ 0\ 2\ 2\rangle$	A_2	0	4

Here we have defined $S(y) \equiv \sinh(y)$ and $C(y) \equiv \cosh(y)$. It is important to note that of the three O_h crystal field states (A_2 , T_1 , T_2) arising from the $J = 3$ atomic multiplet, the T_1 and T_2 are MCD active whereas only the T_1 state gives rise to any MLD.

To proceed further, it is necessary to evaluate the crystal field energies in Eqs 80 and 81 in terms of a set of crystal field parameters. Using the operator equivalent method, the crystal field Hamiltonian for an octahedral field may be written⁷³

$$V_{\text{OCT}} = D[O_4^0 + 5O_4^4]/60 \quad (82)$$

where D is the crystal field (radial) parameter and O_n^m are the rank n spin tensors:

$$\begin{aligned} O_4^0 &= 35J_z^2 - 30J(J+1)J_z^2 + 25J_z^2 - 6J(J+1) + 3J^2(J+1)^2 \\ O_4^4 &= (1/2)[J_+^4 + J_-^4] \end{aligned} \quad (83)$$

Therefore, we obtain the crystal field energies given in Table 16.

Table 16

Crystal Field Energies For The $J=3$ Atomic
State in Octahedral Symmetry

T_1	6D
T_2	-2D
A_2	-12D

As a specific illustration of Eqs. 80 and 81 we let $D = -5.556 \text{ cm}^{-1}$ (total crystal field splitting = 100 cm^{-1}) and g equal to the Lande value of $4/3$. In Figures 10 and 11, the approximate theoretical MCD and MLD saturation curves at 1T are given along with the exact results obtained from a complete diagonalization of the Zeeman-crystal field Hamiltonian, i.e. including the off diagonal Zeeman terms which couple the crystal field basis functions.

As can be seen, the agreement between the exact and approximate theoretical curves is satisfactory. It should be noted that the theory developed (ignoring the off-diagonal Zeeman coupling of the crystal field basis states) necessarily applies only to the case of small ($<0.5T$) magnetic fields, and as such is applicable only to the situation where the temperature dependence of the saturation is investigated. In addition the theory may not accurately predict the saturation behavior for cases where the lowest crystal field component is MCD/MLD inactive especially if this component is Zeeman coupled to higher lying MCD/MLD active components.

Conclusion

It is readily apparent that the MCD/MLD saturation technique should be of great use in studying the crystalline environment of matrix isolated atoms.

Figure 10

Predicted MCD Saturation Curves for a $3d^3$ Ni Atom Embedded in an Octahedral Crystal Field. The Solid Line Corresponds to the Exact Curve While the Dashed Line Corresponds to Eq. 85. $D = -5.556\text{cm}^{-1}$, $g = 4/3$, $B = 1\text{T}$.

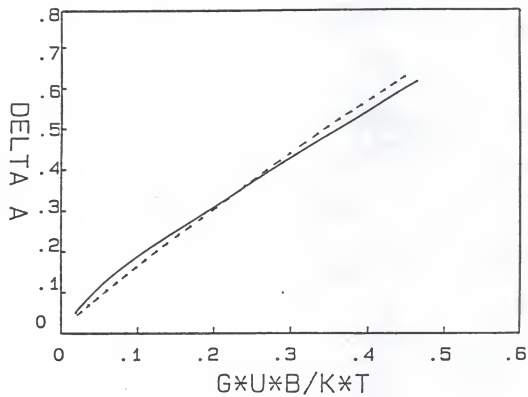
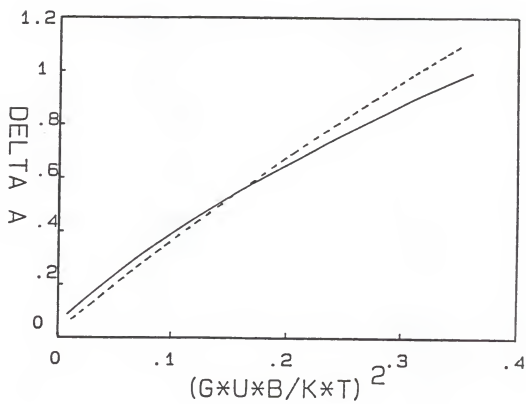


Figure 11

Predicted MLD Saturation Curves for a ${}^3\text{D}^3 \text{Ni}$ Atom Embedded in an Octahedral Crystal Field. The Solid Line Corresponds to the Exact Curve While the Dashed Line Corresponds to Eq. 86. $D = -5.556\text{cm}^{-1}$, $g = 4/3$, $B = 1\text{T}$.



The magnetization curves provide a sensitive probe of both the ground electronic state as well as its site symmetry.

Application to the case of Re matrix isolated in Kr has shown that Re may occupy an octahedral substitutional site, and possesses a large ground state splitting which precludes the observation of any X band ESR.⁷⁴ Further experimental work to verify the theory presented would prove interesting.

CHAPTER 5
MAGNETIC CIRCULAR DICHROISM AND MAGNETIC LINEAR DICHROISM
LINEAR MOLECULE FARADAY PARAMETERS

Introduction

It is well known that magneto-optical spectroscopic methods are powerful tools for understanding the magnetic and electronic properties of atomic and molecular systems.⁷⁵ While magnetic circular dichroism (MCD) spectroscopy has been relatively widely used, the use of other magneto-optical methods such as magnetic linear dichroism (MLD), magnetic circularly polarized luminescence (MCPL) and magnetic linearly polarized luminescence (MLPL) has not been as widespread. Each of these approaches probes different aspects of the system under study and provides much more information than available from simple absorption measurements. Indeed, the combination of MCD and MLD measurements on matrix isolated atomic systems has recently been shown theoretically⁶⁵ and verified experimentally⁷⁶ to provide unambiguous evidence of the total angular momentum change in the transition, simply from the sign of the spectral bands observed. Thus, if the assignment of one electronic state (e.g., the ground state) is known, the other state may readily be assigned.

In the present work a general theory for the MCD and MLD spectroscopy of linear molecules in the low field limit is developed. Specifically, expressions are presented for linear molecules which are randomly oriented and rigidly fixed as in a rare gas matrix. As for the case of atoms, it is shown that the combination of MCD and MLD provides a powerful tool for the assignment of electronic states.

In 1978 Schatz, Mowery, and Krausz⁷⁷ (SMK) presented a thorough discussion of the theory of MCD and MCPL saturation and applied it to linear molecules. In the present work we adopt the approach used by SMK but limit our discussion to only the linear, low magnetic field limit, i.e. the regime where $g\mu_B B/kT \ll 1$. Our interest is not the saturation behavior but rather in the signs of the expected MCD and MLD bands for the transitions between allowed states, i.e., for $\Delta\Omega = 0, \pm 1$ (or $\Delta\Lambda = 0, \pm 1$). In the linear limit, the differential absorbance, $\Delta A = A_L - A_R$ in MCD and $= A_{\parallel} - A_{\perp}$ in MLD can be expressed by certain magneto-optical terms. Because we are interested in molecules whose ground and/or excited electronic states are degenerate, the terms of importance are the Faraday parameters A_1 and C_0 in MCD⁶⁰ and A_2 , C_1 , and G_0 in MLD⁶⁵. The C_0 (MCD) and G_0 (MLD) terms are the most important terms for paramagnetic molecules held at low temperatures: they reflect the difference in Boltzman populations of the two Zeeman split levels of the ground state.

The other terms above result from degeneracies in the excited (and ground) states, but usually only become important at low temperatures for diamagnetic molecules, i.e., ones whose C_0 and G_0 terms are zero.

Our results for the MCD and MLD terms are presented in the following sections. Methods of extraction of these terms from experimental data are then reviewed and a comparison of the two sets of terms is discussed. It is shown that for paramagnetic linear molecules the MCD C_0 terms are negative, absent, and positive for $\Delta\Omega$ transitions of +1, 0, and -1, respectively, while the MLD G_0 terms are negative, positive, and negative for the same order of $\Delta\Omega$'s.

MCD Expressions For Linear Molecules

In this section the MCD parameters, A_1 , and C_0 are derived for linear molecules which are oriented randomly in a matrix. The A_1 and C_0 terms represent the MCD signals which arise from the differential Zeeman shift of the degenerate ground and/or degenerate excited state components involved in the transition and the Boltzman distribution in the Zeeman-split degenerate ground state, respectively.

The mixing of near-lying states by the magnetic field (i.e. the B_0 term) is neglected in the present treatment.

We start with the general expressions for the A_1 , C_0 , and D_0 (dipole strength) terms:

$$A_1 = - \sum_{\alpha} \sum_{\beta} [\langle J\beta | \mu_Z | J\beta \rangle - \langle A\alpha | \mu_Z | A\alpha \rangle] \times \quad (84)$$

$$[|\langle A\alpha | M_- | J\beta \rangle|^2 - |\langle A\alpha | M_+ | J\beta \rangle|^2] / \mu_B d_A \quad (85)$$

$$C_0 = \sum_{\alpha} \sum_{\beta} \langle A\alpha | \mu_Z | A\alpha \rangle [|\langle A\alpha | M_- | J\beta \rangle|^2 - |\langle A\alpha | M_+ | J\beta \rangle|^2] / \mu_B d_A$$

$$D_0 = \sum_{\alpha} \sum_{\beta} |\langle A\alpha | M_Z | J\beta \rangle|^2 / d_A \quad (86)$$

where A is the ground electronic state and α its magnetic sublevels; J is the excited electronic state and β its magnetic sublevels; and μ_Z is the space fixed magnetic moment operator. The transition moment operators are $M_{\pm} = (M_X \pm iM_Y)/\sqrt{2}$ where M_X , M_Y , and M_Z are the cartesian components of the space fixed electric dipole operator.

The degeneracy factor, d_A , for the ground state of a degenerate linear molecule is two.

The above expressions must now be converted from a space-fixed to molecule-fixed coordinate system. Following Schatz⁷⁷ we obtain

$$A_1 = - \sum_{\alpha \beta} [\langle J\beta | \mu_Z | J\beta \rangle - \langle A\alpha | \mu_Z | A\alpha \rangle] \times \Omega_A^J / 2\mu_B \quad (87)$$

$$C_0 = \sum_{\alpha \beta} \langle A\alpha | \mu_Z | A\alpha \rangle \times \Omega_A^J / 2\mu_B \quad (88)$$

$$\begin{aligned} D_0 = & \sum_{\alpha \beta} [\sin^2 \theta |\langle A\alpha | m_+ | J\beta \rangle|^2 + \cos^2 \theta |\langle A\alpha | m_z | J\beta \rangle|^2 \\ & + \sqrt{2} \sin \theta \cos \theta \operatorname{Im} \{ \langle A\alpha | m_+ | J\beta \rangle \langle A\alpha | m_z | J\beta \rangle^* \\ & + \langle A\alpha | m_z | J\beta \rangle \langle A\alpha | m_- | J\beta \rangle^* \}] / 2 \end{aligned} \quad (89)$$

where Im stands for the imaginary part. All of the transition moment operators m_+ , m_- , and m_z are molecule-fixed. The magnetic moment operator μ_Z remains space-fixed and is defined by

$$\mu_Z = \mu_Y \sin \theta + \mu_Z \cos \theta \quad (90)$$

The term Ω_A^J is given by

$$\begin{aligned}
 \Omega_A^J &\equiv |\langle A\alpha | M_- | J\beta \rangle|^2 - |\langle A\alpha | M_+ | J\beta \rangle|^2 \\
 &= \cos\theta [|\langle A\alpha | m_- | J\beta \rangle|^2 - |\langle A\alpha | m_+ | J\beta \rangle|^2] \\
 &\quad + \sqrt{2}\sin\theta \operatorname{Im}\{\langle A\alpha | m_+ | J\beta \rangle \langle A\alpha | m_z | J\beta \rangle^* \\
 &\quad + \langle A\alpha | m_- | J\beta \rangle \langle A\alpha | m_z | J\beta \rangle^*\}
 \end{aligned}
 \tag{91}$$

To develop these expressions specifically for linear molecules we focus on the above magnetic moment and transition moment matrix elements for a doubly degenerate ground state A with Kramer's components $A\alpha$ and $A\alpha'$ where α and α' are the positive and negative components of the Λ or Ω quantum numbers of state A. (Due to an added complexity we defer for the moment those ground states A whose $\Omega = 1/2$.) The magnetic moment matrix elements can be shown to reduce to

$$\langle K\delta | \mu_z | K\delta \rangle = \mp n g_{\parallel}^K \mu_B / 2
 \tag{92}$$

where K may be A or J, $n = \cos\theta$, $g_{\parallel}^K$ is the parallel component of the Kth (A or Jth) state Lande g tensor, and the positive (negative) sign holds for the negative (positive) Kramer's components δ' (δ).

$\Delta\Omega = +1$ Transitions

For the case in which the Jth state Ω (or Λ) quantum number is one higher than the Ath state Ω (or Λ) i.e. for the transition $\Delta\Omega(\Lambda) = +1$, all of the matrix elements involving the m_z transition moment operator vanish by symmetry. The only surviving transition moment matrix elements are

$$|\langle A\alpha | m_- | J\beta \rangle|^2 = |\langle A\alpha' | m_+ | J\beta' \rangle|^2 \equiv |\bar{m}|^2 \quad (93)$$

where the β ($=\alpha+1$) and β' ($=\alpha'-1$) components are defined analogously to α and α' above. Substituting into Eqs.(87) - (91) we find that

$$A_1 = -(g_{\parallel}^A - g_{\parallel}^J)n^2|\bar{m}|^2/2 \quad (94)$$

$$C_0 = -g_{\parallel}^A n^2|\bar{m}|^2/2 \quad (95)$$

Now averaging these expressions over all angles to account for the random orientation of all molecules gives

$$\bar{A}_1 = -(g_{\parallel}^A - g_{\parallel}^J) |\bar{m}|^2/6 \quad (96)$$

$$\bar{C}_0 = -g_{\parallel}^A |\bar{m}|^2/6 \quad (97)$$

$$\bar{D}_0 = |\bar{m}|^2/3 \quad (98)$$

Finally, dividing by the angle averaged dipole strength, $\bar{D}_0$, gives

$$\bar{A}_1/\bar{D}_0 = -(g_{\parallel}^A - g_{\parallel}^J)/2 \quad (99)$$

$$\bar{C}_0/\bar{D}_0 = -g_{\parallel}^A/2 \quad (100)$$

$\Delta\Omega = -1$ Transitions

For the case in which the Jth state $\Omega(\Lambda)$ quantum number is one lower than the Ath state $\Omega(\Lambda)$, i.e. for the transition $\Delta\Omega = -1$, the analogous expressions are

$$\bar{A}_1/\bar{D}_0 = +(g_{\parallel}^A - g_{\parallel}^J)/2 \quad (101)$$

$$\bar{C}_0/\bar{D}_0 = +g_{\parallel}^A/2 \quad (102)$$

$\Delta\Omega = 0$ Transitions

For the transition in which $\Delta\Omega (\Lambda) = 0$, all transition moment matrix elements involving m_+ and m_- vanish. Thus Ω_A^J vanishes, as does A_1 and C_0 . However, D_0 does not. The latter survives since the second term in Eq.(89) is nonzero.

$\Omega = 1/2 \rightarrow \Omega = 1/2$ or $3/2$ Transitions

The analysis for transitions involving ground A states with $\Omega = 1/2$ and excited J states with $\Omega = 1/2$ or $3/2$ is complicated by the fact that the Zeeman Hamiltonian, $-\mu_B B$, is not diagonal in the ground state $|+1/2\rangle$, $|-1/2\rangle$ basis. The Zeeman matrix is (in units of $\mu_B B$)

$$\begin{array}{cc}
 & \begin{array}{cc} |+1/2\rangle & |-1/2\rangle \end{array} \\
 \begin{array}{c} |+1/2\rangle \\ \\ |-1/2\rangle \end{array} & \begin{bmatrix} ng_{\parallel}/2 & lg_{\perp}/2 \\ l^*g_{\perp}/2 & -ng_{\parallel}/2 \end{bmatrix}
 \end{array} \quad (103)$$

where $g_{\perp} = -\sqrt{2} \langle +1/2 | \mu_{+} | -1/2 \rangle \mu_B$, $l = -i \sin \theta$ and $g_{\parallel}$ and n are as given previously. Diagonalizing this matrix yields the following eigenstates and eigenvalues

$$|A_{+}\rangle = c_1 | +1/2 \rangle + c_2 | -1/2 \rangle \quad \text{with } E_{+} = g_{\perp}^A V \mu_B / 2 \quad (104)$$

$$|A_{-}\rangle = c_2 | +1/2 \rangle - c_1 | -1/2 \rangle \quad \text{with } E_{-} = -g_{\perp}^A V \mu_B / 2 \quad (105)$$

where $c_2 c_1^{*} = (1-n^2)/2Vl$, $|c_2|^2 - |c_1|^2 = -nS/V$, $S = g_{\parallel}^A / g_{\perp}^A$ and $V = [n^2(S^2-1) + 1]^{1/2}$. Since now $|\langle \pm 1/2 | m_{\mp} | \pm 3/2 \rangle|^2 = |m|^2$ Eqs.(87)-(91) lead to

$$\bar{A}_1 / \bar{D}_0 = -(g_{\parallel}^A - g_{\parallel}^J) / 2 \quad (106)$$

$$\bar{C}_0 / \bar{D}_0 = -g_{\parallel}^A / 2 \quad (107)$$

for the A state $\Omega = 1/2$ and the J state $\Omega = 3/2$.

Note that these results are identical to Eqs.(99) and (100) for the general $\Delta\Omega = +1$ case. In addition, the $\Omega = 3/2$ to $\Omega = 1/2$ results are the same as the general $\Delta\Omega = -1$ case (Eqs.(101) and (102)).

The corresponding expressions for the $\Omega = 1/2$ to $\Omega = 1/2$ case for randomly oriented linear molecules are as follows:

$$\bar{A}_1 = (g_{\parallel}^A + g_{\parallel}^J) |\bar{m}|^2 / 6 \quad (108)$$

$$\bar{C}_0 = g_{\parallel}^A |\bar{m}|^2 / 6 \quad (109)$$

$$\bar{D}_0 = (|\bar{m}|^2 + |\bar{m}_z|^2) / 3 \quad (110)$$

where $|\bar{m}|^2 = |\langle \pm 1/2 | m_{\pm} | \mp 1/2 \rangle|^2$ and $|\bar{m}_z|^2 = |\langle \pm 1/2 | m_z | \pm 1/2 \rangle|^2$.

Notice that although this particular transition appears to fall under the broad classification of $\Delta\Omega = 0$ transitions, the A_1 and C_0 expressions are not zero here and the D_0 expression is different (compare Eqs.(110) and (98)).

MLD Expressions For Linear Molecules

In this section the magnetic linear dichroism (MLD) Faraday parameters analogous to the previously derived MCD parameters are developed for randomly oriented linear molecules. The pertinent parameters are A_2 , C_1 , and G_0 . They are defined in general terms as

$$A_2 = \sum_{\alpha} \sum_{\beta} [\langle J\beta | \mu_z | J\beta \rangle - \langle A\alpha | \mu_z | A\alpha \rangle]^2 \Gamma_A^J / 2\mu_B^2 \quad (111)$$

$$C_1 = - \sum_{\alpha} \sum_{\beta} [\langle J\beta | \mu_Z | J\beta \rangle - \langle A\alpha | \mu_Z | A\alpha \rangle \langle A\alpha | \mu_Z | A\alpha \rangle \Gamma_A^J / 2\mu_B^2] \quad (112)$$

$$G_0 = \sum_{\alpha} \sum_{\beta} | \langle A\alpha | \mu_Z | A\alpha \rangle |^2 \Gamma_A^J / 4\mu_B^2 \quad (113)$$

where

$$\Gamma_A^J \equiv | \langle A\alpha | M_Z | J\beta \rangle |^2 - [| \langle A\alpha | M_X | J\beta \rangle |^2 + | \langle A\alpha | M_Y | J\beta \rangle |^2] / 2 \quad (114)$$

Note that we have divided the expressions for A_2 , C_1 , and G_0 from Ref 65 by μ_B^2 to be consistent with the MCD equations used. Converting to molecule fixed quantities we obtain

$$\begin{aligned} \Gamma_A^J = & (1/2)(3\cos^2\theta - 1)[| \langle A\alpha | m_Z | J\beta \rangle |^2 - \{ | \langle A\alpha | m_+ | J\beta \rangle |^2 \\ & + | \langle A\alpha | m_- | J\beta \rangle |^2 \} / 2] + (3\sqrt{2}/2)\sin\theta\cos\theta \{ \langle A\alpha | m_+ | J\beta \rangle \langle A\alpha | m_Z | J\beta \rangle^* \\ & + \langle A\alpha | m_Z | J\beta \rangle \langle A\alpha | m_- | J\beta \rangle^* \} \end{aligned} \quad (115)$$

As defined previously, μ_Z in Eqs.(111) - (113) and M_Z , M_X , and M_Y in Eq.(114) are space-fixed, while the operators in Γ_A^J (cf. (115)) are molecule-fixed.

$\Delta\Omega = \pm 1$ Transitions

For all transitions, $\Delta\Omega = \pm 1$, except $1/2 \leftrightarrow 3/2$, the m_z transition moment matrix elements are equal to zero. Designating the symmetry unique m_+ and m_- transition moment matrix elements as m (cf. Eq.(93)) and using the magnetic moment matrix elements as given in Eq.(92), we find

$$\bar{A}_2/\bar{D}_0 = -(g_{\parallel}^A - g_{\parallel}^J)^2/20 \quad (116)$$

$$\bar{C}_1/\bar{D}_0 = -(g_{\parallel}^A - g_{\parallel}^J)g^A/20 \quad (117)$$

$$\bar{G}_0/\bar{D}_0 = -(g_{\parallel}^A)^2/40 \quad (118)$$

with again $\bar{D}_0 = |\bar{m}|^2/3$. Note that for low temperatures where the MLD signal is expected to be dominated by the G_0 term, negatively-signed bands are predicted for both $\Delta\Omega = \pm 1$ transitions. This is in contrast to the prediction for the MCD C_0 terms given in Eqs.(100) and (102) where for $\Delta\Omega = +1$ transitions a negative MCD band and for $\Delta\Omega = -1$ transitions a positive MCD band is predicted.

$\Delta\Omega = 0$ Transitions

Next we consider the case of $\Delta\Omega = 0$. (The $1/2 \rightarrow 1/2$ case will be treated separately.) The only nonzero transition moments are $\langle A\alpha | m_z | A\alpha \rangle = \langle A\alpha' | m_z | A\alpha' \rangle \equiv m_z$. Substituting into Eqs.(111)-(115) yields

$$\bar{A}_2/\bar{D}_0 = (g_{\parallel}^A - g_{\parallel}^J)^2/10 \quad (119)$$

$$\bar{C}_1/\bar{D}_0 = (g_{\parallel}^A - g_{\parallel}^J)g_{\parallel}^A/10 \quad (120)$$

$$\bar{G}_0/\bar{D}_0 = (g_{\parallel}^A)^2/20 \quad (121)$$

and $\bar{D}_0 = |\bar{m}_z|^2/3$. Thus, at low temperatures the MLD signal is expected to be positive since the most important low temperature term, G_0 , is positive.

$\Omega = 1/2 \rightarrow 1/2$ or $3/2$ Transitions

As discussed above, the analysis of transitions originating from the $\Omega = 1/2$ states are complicated due to off diagonal Zeeman coupling between the $+1/2$ and $-1/2$ sublevels. Using the same approach as adopted for the MCD derivation, we

obtain for the $\Omega = 1/2 \rightarrow \Omega = 3/2$ case

$$\bar{A}_2/\bar{D}_0 = -[(g_{\parallel}^A - g_{\parallel}^J)^2 - (g_{\perp}^A)^2]/20 \quad (122)$$

$$\bar{C}_1/\bar{D}_0 = -[g_{\parallel}^A(g_{\parallel}^A - g_{\parallel}^J) - (g_{\perp}^A)^2]/20 \quad (123)$$

$$\bar{G}_0/\bar{D}_0 = -[(g_{\parallel}^A)^2 - (g_{\perp}^A)^2]/40 \quad (124)$$

Here it is unfortunately not possible to predict the sign of the expected MLD signal since the quantities in square brackets may be positive or negative depending on the relative magnitudes of $g_{\parallel}^A$ and $g_{\parallel}^J$ versus $g_{\perp}^A$.

For the case with $\Omega = 3/2 \rightarrow \Omega = 1/2$ Eq.(135) for $\bar{A}_2/\bar{D}_0$ holds with A and J interchanged and Eqs.(117) and (118) hold for the important C_1/D_0 and G_0/D_0 terms.

The MLD expressions for the $\Omega = 1/2 \rightarrow \Omega = 1/2$ case are given below.

$$\bar{A}_2 = [2|m_z|^2[(g_{\parallel}^A - g_{\parallel}^J)^2 - 2\{(g_{\perp}^A)^2 + (g_{\perp}^J)^2\}] - |m|^2[(g_{\parallel}^A + g_{\parallel}^J)^2 - \{(g_{\perp}^A)^2 + (g_{\perp}^J)^2\}]]/60 \quad (125)$$

$$\bar{G}_0 = [2|\bar{m}_z|^2\{(g_{\parallel}^A)^2 - 2(g_{\perp}^A)^2\} - |m|^2\{(g_{\parallel}^A)^2 - (g_{\perp}^A)^2\}]/120 \quad (126)$$

$$\bar{C}_1 = [|\bar{m}_z|^2\{(g_{\parallel}^A)^2 - 2(g_{\perp}^A)^2 - g_{\parallel}^A g_{\parallel}^J\} - (|m|^2/2)\{(g_{\parallel}^A)^2 - (g_{\perp}^A)^2 + g_{\parallel}^A g_{\parallel}^J\}]/60 \quad (127)$$

where for the sake of simplicity, we have set the ratios of the g factors, $g_{\parallel}^A/g_{\perp}^A$ and $g_{\parallel}^J/g_{\perp}^J$, equal to each other.

Extraction of the MCD and MLD Terms Via Moment Analysis

The use of the method of moments in the evaluation of MCD data has been effective in recent years to extract information on excited state spin-orbit coupling constants, Jahn-Teller activity, etc.^{29-33,63,66,78} The use of moments with MLD data has however not been exploited, although the appropriate expressions have been reported.⁶⁵ The moments for MCD or MLD and absorption are defined as:

$$\langle A \rangle_n^{E^0} = \int (A/E)(E - E^0)^n dE \quad (128)$$

$$\langle \Delta A \rangle_n^{E^0} = \int (\Delta A/E)(E - E^0)^n dE \quad (129)$$

where E^0 is the center of gravity of the absorption band and n is the order of the moment. Expressing the magnetic field strength as B , the sample concentration as c and the path length as y , the moments for MCD and MLD are given by

$$\begin{aligned}
\langle A \rangle_0 &= \tau D_0 c \gamma \\
\langle \Delta A^{\text{MCD}} \rangle_0 &= \tau (B_0 + C_0/kT) B c \gamma \mu_B \\
\langle \Delta A^{\text{MCD}} \rangle_1 &= \tau A_1 B c \gamma \mu_B \\
\langle \Delta A^{\text{MLD}} \rangle_0 &= \tau (F_0 + G_0/kT) B^2 c \gamma \mu_B^2 / kT \\
\langle \Delta A^{\text{MLD}} \rangle_1 &= \tau (B_1 + C_1/kT) B^2 c \gamma \mu_B^2 \\
\langle \Delta A^{\text{MLD}} \rangle_2 &= \tau [A_2 + p(F_0 + G_0/kT)/kT] B^2 c \gamma \mu_B^2
\end{aligned} \tag{130}$$

The terms not discussed here (B_0 , F_0 , B_1 , and p) are usually small; they are defined elsewhere. In practice, each of the MCD or MLD moments are divided by the zeroth order absorption moment to remove any dependence on the sample concentration or path length. The MCD C_0 term is obtained from the slope of a $\langle \Delta A^{\text{MCD}} \rangle_0 / \langle A \rangle_0$ vs. inverse temperature plot while the MCD A_1 term is gotten from a similar $\langle \Delta A^{\text{MCD}} \rangle_1 / \langle A \rangle_0$ plot. The MLD A_2 term may be obtained from the relation

$$\langle \Delta A^{\text{MLD}} \rangle_2 = \tau B^2 c \gamma \mu_B^2 A_2 + p \langle \Delta A^{\text{MLD}} \rangle_0 \tag{131}$$

A plot of $\langle \Delta A^{\text{MLD}} \rangle_2$ vs. $\langle \Delta A^{\text{MLD}} \rangle_0$ will yield a straight line whose intercept gives A_2 . The C_1 term may be obtained from the slope of a $\langle \Delta A^{\text{MLD}} \rangle_1 / \langle A \rangle_0 B^2$ vs. $1/T$ plot and the G_0 term from the slope of a $\langle \Delta A^{\text{MLD}} \rangle_0 T / \langle A \rangle_0 B^2$ vs. $1/T$ plot.

With the digital data acquisition available in most modern

spectrometers, the calculation of any of these moments is a relatively simple task.

Discussion

The major results presented here are summarized in Tables 17 and 18. Table 17 contains the expressions of importance for paramagnetic molecules. It can be seen that MCD alone is capable of providing definitive information on the assignment of the transition since for $\Delta\Omega = -1, 0$, and $+1$, C_0/D_0 is predicted to be positive, absent, and negative. On the other hand, the prediction for MLD is the same (negative) for both $\Delta\Omega = \pm 1$ and is different (positive) for $\Delta\Omega = 0$.

Table 18 shows that for transitions between ground and excited states whose g factors are similar the $A_1(\text{MCD})$, $C_1(\text{MLD})$, and $A_2(\text{MLD})$ terms will be small. This situation arises since each of these terms depends upon the quantity $(g_{\parallel}^A - g_{\parallel}^J)$. Conversely for a diamagnetic molecule ($g_{\parallel}^A = 0$) with the allowed transitions $^1\Sigma \rightarrow ^1\Sigma$ or $^1\pi$ the A_1 term will be zero and positive, the C_1 term will be zero and zero, and the A_2 term will be zero and negative for $\Delta\Omega = 0$ and $+1$, respectively.

Previous reports on the absorption and MCD spectra of TaO isolated in Ar matrices demonstrate that transitions from the ground $^2\Delta_{3/2}$ state to $\Omega = 1/2, 3/2$, and $5/2$ excited states obey the C_0 sign predictions presented in Table 17.

It would be of interest to determine whether the MLD G_0 predictions also hold.

The results presented here are expected to be useful for the assignment of excited and ground electronic states of matrix isolated diatomic as well as linear polyatomic homo and heteronuclear transition metal clusters. While good progress has been made via ESR studies⁷⁹, on the ground states of these species, the electronic excited states of many remain unknown.

Table 17

Calculated $\bar{C}_0/\bar{D}_0$ and $\bar{G}_0/\bar{D}_0$ terms for randomly oriented paramagnetic linear molecules.

$\Delta\Omega$	$\bar{C}_0/\bar{D}_0$	$\bar{G}_0/\bar{D}_0$
-1	$+g_{\parallel}^A/2$	$-(g_{\parallel}^A)^2/40$
0 ^a	none	$+(g_{\parallel}^A)^2/20$
+1	$-g_{\parallel}^A/2$	$-(g_{\parallel}^A)^2/40$

^a The $\Omega = 1/2 \rightarrow 1/2$ case is special; cf. text.

Table 18

Calculated $\bar{A}_1/\bar{D}_0$, $\bar{C}_1/\bar{D}_0$, and $\bar{A}_2/\bar{D}_0$ terms for
randomly oriented linear molecules

	<u>MCD</u>		<u>MLD</u>	
$\Delta\Omega$	$\bar{A}_1/\bar{D}_0$	$\bar{C}_1/\bar{D}_0$	$\bar{A}_2/\bar{D}_0$	
-1^a	$+(g_{\parallel}^A - g_{\parallel}^J)/2$	$-(g_{\parallel}^A - g_{\parallel}^J)g_{\parallel}^A/20$	$-(g_{\parallel}^A - g_{\parallel}^J)^2/20$	
0^b	none	$+(g_{\parallel}^A - g_{\parallel}^J)g_{\parallel}^A/10$	$+(g_{\parallel}^A - g_{\parallel}^J)^2/10$	
$+1^c$	$-(g_{\parallel}^A - g_{\parallel}^J)/2$	$-(g_{\parallel}^A - g_{\parallel}^J)g_{\parallel}^A/20$	$-(g_{\parallel}^A - g_{\parallel}^J)^2/20$	

^a The $\Omega = 3/2 \rightarrow 1/2$ case is special; cf. text.

^b The $\Omega = 1/2 \rightarrow 1/2$ case is special; cf. text.

^c The $\Omega = 1/2 \rightarrow 3/2$ case is special; cf. text.

CHAPTER 6 G FACTOR SUM RULE

In the past, the identification of specific multiplet J values within an atomic Russell-Saunders term was often accomplished by measuring the Zeeman splitting of several optical bands involving the multiplet and comparing with the expected theoretical value found using the Lande g-factor formula. In the course of magnetic circular dichroism studies on matrix isolated atomic species we have found a g-factor sum rule which apparently has not been recognized previously.⁸⁰ We present the rule here and provide examples, one from each of the three rows of transition metals, which confirm our finding. Finally, we use the rule to determine a g factor for a specific multiplet of V which is currently unknown experimentally.

In the presence of spin-orbit coupling, the orbital and spin angular momenta of an atom couple to generate an effective magnetic moment given by⁴³

$$\vec{\mu} = -g_J(L, S)\mu_B \vec{J} \quad (132)$$

where μ_B is the Bohr magneton, $\vec{J}$ is the total angular momentum and $g_J(L,S)$ is the Lande g factor given by⁴³

$$g_J(L,S) = \quad (133)$$

$$g_1 + (g_s - g_1)[J(J+1) + S(S+1) - L(L+1)]/2J(J+1)$$

The free spin g factor g_s is approximately 2.0023 and $g_1 \approx 1$. The average g value for all the J multiplets arising from a given Russell-Saunders term may be defined as

$$\bar{g} = \sum_J g_J(L,S)/N \quad (134)$$

where N is the number of terms in the summation, and is equal to the smaller of $2L + 1$ and $2S + 1$. Substituting (133) into (134) yields

$$\bar{g} = (g_s + g_1)/2 +$$

$$(g_s - g_1)[S(S+1) - L(L+1)]/2N \sum_J 1/J(J+1) \quad (135)$$

Evaluation of the summation leads to

$$\sum_J 1/(J(J+1)) = \pm N/[L(L+1) - S(S+1)] \quad (136)$$

where the positive sign holds for $L > S$ and the negative sign for $S > L$. Thus, we find the following interesting result for the average g

$$\bar{g} = \begin{cases} g_L & \text{for } L > S \\ g_S & \text{for } S > L \end{cases} \quad (137)$$

Hence the average g value reduces to the pure spin or orbital value depending upon the relative magnitudes of L and S . Note, for the case of $L = S$, $g_J(L, L) = 3/2$ except for $g_0(L, L)$ which is indeterminate.

In Table 19 are given experimental and theoretical $\bar{g}$ values ($g_S \approx 2, g_L \approx 1$), determined from (147) and (150) respectively, for a number of excited terms of V, Mo, and Re³⁵. The root mean square (RMS) deviations are 0.05, 0.08, and 0.20, respectively. As expected, the RMS deviations increase as one proceeds from the first to the third row transition elements, reflecting the increasing inter-term SO coupling, i.e. departure from Russell-Saunders coupling.

Table 19

Comparison of Experimental and Theoretical g Values
for Excited Terms of Atomic V, Mo, and Re

V			Mo			Re		
Term	g_{exp}	g_{theor}	Term	g_{exp}	g_{theor}	Term	g_{exp}	g_{theor}
a^4F	0.97	1	a^7S	1.99	2	a^4P	1.71	2
a^6D	1.95	2	a^7S	1.98	2	a^6D	1.73	2
a^4D	0.98	1	a^5G	1.00	1	a^4G	1.18	1
a^4P	1.95	2	a^5P	1.95	2	a^4D	1.26	1
a^2G	1.00	1	a^3D	1.22	1	z^8P	1.99	2
a^2P	0.92	1	a^3G	1.01	1	a^2F	1.10	1
a^2D	1.07	1	a^3F	.954	1	a^2G	1.11	1
a^4H	0.97	1	a^3H	1.08	1	a^2D	0.98	1
b^4P	1.94	2	a^3I	0.99	1	a^2I	1.05	1
a^2H	0.98	1	z^7P	1.98	2	z^6P	1.97	2
b^4F	0.99	1	b^3D	1.18	1	z^4P	1.83	2
z^6G	0.96	1	b^3F	1.02	1	z^6G	1.13	1
a^4G	0.99	1	b^3G	1.07	1	x^6P	1.56	2
z^6D	1.93	2	z^5P	2.00	2	z^4D	1.25	1

The rule may be used to determine the g factor for a particular multiplet within a term whose other multiplet g values are known experimentally. For example, for the $V u^4 D$ state, g factors are known for the $J = 7/2, 5/2,$ and $3/2$ multiplets but not the $J=1/2$. The g factor for the $u^4 D_{1/2}$ multiplet calculated from the g value equation is 0.23 ± 0.09 while the value calculated from the Lande formula is zero. The error quoted here is determined by a propagation of errors approach on Eq.134. Namely $\Delta g_J(L,S) = N^{1/2} \Delta g$, where Δg is the rms deviation quoted above. This difference, which is outside the expected error limits, signifies a departure from the Russell-Saunders limit for this term.

The question arises as to which of these g factors is the more reliable. If we rewrite (134) explicitly for the experimental Lande factors, $g_J^e(L,S)$, we obtain

$$\bar{g}_{\text{exp}} = 1/N \sum_J g_J^e(L,S) = \bar{g} \pm a \quad (138)$$

where the 'a' corrects for the departure from the exact theoretical g . If we now partition $g_J^e(L,S)$ into a Lande $g_J(L,S)$ and a correction δg_J (which includes the departure from a RS coupling and/or experimental error) we obtain

$$g_J^e(L,S) = g_J(L,S) + \delta g_J \quad (139)$$

Hence it follows that the difference between the exact g factor and that predicted by (133) is given by

$$-\sum_J' \delta g_J \pm Na \quad (140)$$

The prime indicates a sum over the $N-1$ terms for which $g_J^e(L,S)$ and hence δg_J are experimentally known. The difference between the exact g and that calculated from (138) (with $a=0$, i.e. the sum rule) is $\pm Na$. Since the ' Na ' term as well as the sum in (140) may be positive or negative, there is no way of knowing which difference is smaller. Hence it is not possible to determine a priori whether the g factor computed from the sum rule is more reliable than that obtained from the Lande equation. Nevertheless, when used in conjunction with the Lande equation, the sum rule may find its greatest usefulness in signalling the admixture via spin-orbit coupling of other states into the multiplets of the term under study.

We can extend the above treatment to take into account nuclear hyperfine coupling. In this case, the electronic angular momentum, J , is coupled to the nuclear angular momentum, I , to yield the total angular momentum, F where $F = |J-I|, |J-I|+1, \dots, J+I$. Using a simple vector

coupling model, we obtain the following expression for g_F

$$g_F = g_J[F(F+1) + J(J+1) - I(I+1)]/[2F(F+1)] \\ - (g_I m/M)[F(F+1) + I(I+1) - J(J+1)]/[2F(F+1)] \quad (141)$$

Here, g_I is the nuclear g factor (≈ 1) and m (M) is the electron (nuclear) mass. Obviously, the second term is virtually insignificant. Summing over all F for a given J and I , and dividing by the number of F values, N' , we find

$$\bar{g}_F \equiv \sum_F g_F / N' = \begin{cases} g_J & J > I \\ (m/M)g_I & I > J \end{cases} \quad (142)$$

Hence the average g value, g_F , reduces to the pure electronic and nuclear values depending upon the relative magnitudes of J and I . It is interesting to note that for the case $I > J$, $g_F \approx 0$ since the nuclear mass, M , is so much greater than the electron rest mass, m . Unfortunately, sufficient experimental data to verify the above sum rule does not appear to be available.

CHAPTER 7 ISOTOPOMERIC CLUSTERS

Linear Molecules

The use of isotopically labelled molecules in vibrational spectroscopy is a well established method of unravelling complicated spectra.⁸¹ Specifically, in the study of matrix isolated clusters, knowledge of the number of possible isotopomers is key to identifying the cluster size as well as geometry.⁸² We derive here a simple formula for the number of isotopomers of any linear single element cluster containing two possible isotopes (ex. ^{12}C and ^{13}C). Following this, a general formula applicable to any cluster symmetry is presented.

For linear clusters, the total number of isotopomers, N_T , can be partitioned into symmetric and asymmetric structures.

$$N_T = N_S + N_A \quad (143)$$

In addition, the total can be represented as

$$N_T = 2^n - N_A \quad (144)$$

where the 2^n represents the 2 isotopic possibilities for each of n atoms and the N_A term corrects for the fact that the asymmetric structures are counted twice (for example $^{13}\text{C}-^{12}\text{C}-^{12}\text{C}-^{12}\text{C}$ and $^{12}\text{C}-^{12}\text{C}-^{12}\text{C}-^{13}\text{C}$). Solving we obtain

$$N_T = 2^{n-1} + N_S/2 \quad (145)$$

Now it remains to determine N_S as a function of n . For n even, we find

$$N_S = \sum_k \binom{n/2}{k} = 2^{n/2} \quad (146)$$

where the binomial coefficient represents the number of symmetric structures with k isotopic substitutions on each half ($n/2$ atoms) of the molecule. Similarly for n odd we obtain

$$N_S = 2 \sum_k \binom{(n-1)/2}{k} = 2^{(n+1)/2} \quad (147)$$

where the 2 represents the fact that the atom on the plane of symmetry may be of either isotope regardless of the distribution on isotopes in the rest of the cluster.

Combining Eqs. (145)-(147), we obtain the final results

$$N_T(n \text{ even}) = 2^{n-1} + 2^{n/2} - 1 \quad (148)$$

$$N_T(n \text{ odd}) = 2^{n-1} + 2^{(n-1)/2} \quad (149)$$

Hence for carbon clusters containing ^{12}C and ^{13}C we find the results given in Table 20. As can be seen the possible number of isotopomers increases rapidly with increasing n . As a matter of fact, the number of isotopomers for n odd is simply twice the number of isotopomers for the next smaller (even) cluster, i.e.

$$N_T(n_{\text{even}} + 1) = 2N_T(n_{\text{even}}) \quad (150)$$

Hence the density of vibrational bands in the IR or Raman provides important information regarding the size of a matrix isolated cluster.

General Symmetry Case

Next we attempt to generalize the preceeding results to the general symmetry case. Our starting point is the Polya enumeration method.⁸³ The cycle index $Z(H)$ is defined as

$$Z(H) = (1/h) \sum_i h_i (f_1^{1_1} f_2^{1_2} \dots f_p^{1_p})_i \quad (151)$$

Table 20

Total Isotopomers, N_T , as a Function of Cluster Size, n

n	N_T
1	2
2	3
3	6
4	10
5	20
6	36
7	72
8	136
9	272
10	528

where H is the molecular symmetry group (or rotational subgroup) of order h , h_i is the number of symmetry elements in class i ($\sum h_i = h$), and $f_k^{l_k}$ are variables with l_k equal to the number of cycles of order k associated with the symmetry elements of the group. For example, if we consider the C_5 cluster of D_{5h} symmetry, the results in Table 21 are obtained. Therefore the cycle index is given by

$$Z_{(D_5)} = (1/10)[f_1^5 + 4f_5^1 + 5f_1^1 f_2^2] \quad (152)$$

If we now replace $f_k^{l_k}$ by $(1 + x^k)^{l_k}$ we obtain the polynomial

$$Z_{(D_5)} = 1 + x + 2x^2 + 2x^3 + x^4 + x^5 \quad (153)$$

such that the coefficient of x^n is the number of isotopomers in which n ^{12}C (for example) have been replaced by n ^{13}C . As a result, there is 1 isotopomer containing zero ^{13}C , 1 isotopomer containing one ^{13}C , etc. for a total of 8.

We can simplify the computation of the total number of isotopomers by summing the coefficients in the cycle index polynomial. Each term of Eq. (151) contains products of the form $f_1^{l_1} \dots f_p^{l_p}$ where the number of terms in the product string is equal to the number of different cycle lengths.

Table 21
Construction of Cycle Index for C_5 (D_{5h}) Using the
Rotational Subgroup, D_5

Classes	Representative Permutation	$h_1 f_1^{1_1} \dots f_p^{1_p}$
E	(1)(2)(3)(4)(5)	$1 f_1^5$
$2C_5$	(12345)	$2 f_5^1$
$2C_5^2$	(13524)	$2 f_5^1$
$5C_2$	(1)(25)(34)	$5 f_1^1 f_2^2$

Applying the binomial theorem

$$f_k^{1_k} = (1 + x^k)^{1_k} = \sum_a \binom{1_k}{a} x^{ka} \quad (154)$$

and hence the number of terms in the final polynomial arising from $f_k^{1_k}$ is therefore

$$\sum_a \binom{1_k}{a} = 2^{1_k} \quad (155)$$

For products such as $f_k^{1_k} f_{k'}^{1_{k'}}$ we obtain

$$\sum_a \binom{1_k}{a} \sum_{a'} \binom{1_{k'}}{a'} = 2^{1_k + 1_{k'}} \quad (156)$$

and in general we obtain $2^{\sum 1_k}$ where the summation is over all cycles for a particular class. (Note, all symmetry elements within a given class have the same cycle structure.) As a result, the total number of isotopomers, N_T , is given by

$$N_T = (1/h) \sum_i h_i 2^{(\sum 1_k)_i} \quad (157)$$

This can be simplified further by noting that $(\sum 1_k)_i$ is simply equal to the number of cycles in class i , L_i .

Hence

$$N_T = (1/h) \sum_i \chi_i 2L_i \quad (158)$$

i

To apply Eq. (158), it is useful to recognize that L_i is the number of sets of nuclei rendered symmetry equivalent by the symmetry operations in class i . For example, for the C_4 cluster of C_{3v} symmetry (C_3 rotational subgroup) we obtain trivially $L_E = 4$ for the identity ($L_E = n$ in general) and $L_{C_3} = 2$ for the C_3 class. Hence the number of isotopomeric C_4 clusters is given by $(1/3) \times [(1)2^4 + (2)2^2] = 8$.

In fact, since we may always work in the rotational subgroup, each class, i , is associated with a symmetry element C_i corresponding to a rotation by $360/i$ degrees. If there are m_i atoms (out of a total of n) on the C_i axis, then the remaining $n - m_i$ atoms are partitioned into $(n - m_i)/i$ different sets (cycles) of symmetry equivalent nuclei. Therefore we find

$$L_i = m_i + (n - m_i)/i \quad (159)$$

It is important to note that for the general rotation C_i^j in which i is divisible by j , one should use i/j in place of i in the denominator of Eq.(159). For example, for the case $C_6^3 = C_2$ we have $i = 2$ (not 6) whereas C_5^2 yields $i = 5$.

We can gain further insight into this equation by noting that 2^{L_i} is the number of isotopomers with the symmetry associated with class i . For the C_4 cluster discussed above, there are $2^2 = 4$ isotopomers with a C_3 axis. In other words, the C_3 operation partitions the atoms into 2 sets ($L_{C_3} = 2$): an apex atom and a basal set of 3 atoms. Each of these 2 sets can be all ^{12}C or ^{13}C and hence there are 4 isotopomers with a C_3 axis. The identity on the other hand partitions the atoms into 4 sets (each containing 1 atom); i.e. it does not render any of the atoms equivalent. Hence each atom can be ^{12}C or ^{13}C and we have $2^4 = 16$ structures, many of which are redundant. Therefore the correct number of isotopomers is just an average of 2^{L_i} where the average is taken over all of the classes in the appropriate symmetry group or rotational subgroup. In compact notation,

$$N_T = \langle 2^{L_i} \rangle \quad (160)$$

Finally, we demonstrate that Eq. (158) (or (160)) reduces to Eqs. (148) and (149) for the case of a linear molecule. To avoid the problem of working with the infinite order $D_{\infty h}$ group, we distort the molecule by a small amount as follows. For the case of n even, the molecular chain is bent in a zig zag fashion such that one end is up and the other down, ie C_{2h} symmetry. For the case of n odd, we again bend the chain of atoms such that both ends are pointing in the same direction,

ie C_{2v} symmetry. This does not change the number of isotopomers, and allows us to work in the C_2 rotational subgroup. For the case of n even, $L_E = n$ and $L_{C_2} = n/2$ while for n odd $L_E = n$ and $L_{C_2} = (n + 1)/2$. Hence using Eq. (158) with $h = 2$ and $h_i = 1$ we obtain Eqs. (148) and (149).

We can extend the above treatment to include the case of more than two possible isotopes. In fact for a single element cluster where N isotopes are considered Eq.(158) becomes

$$N_T = (1/h) \sum_i h_i N_i^{L_i} \quad (161)$$

$$= \langle N_i^{L_i} \rangle$$

For example, if we look at a 3 atom cluster of C_{2v} symmetry (C_2 rotational subgroup) where 3 isotopes are considered there are $(1/2)[3^3 + 3^2] = 18$ possible isotopomers.

It is also a simple matter to treat the case of a molecule or cluster containing more than one element. Since each of the elemental subsets are independent of each other we have

$$N_T = \pi \left[(1/h) \sum_i h_i N_j^{L_i(j)} \right] \quad (162)$$

$$= \pi \langle N_j^{L_i(j)} \rangle$$

where the product is taken over each element, j , of which N_j isotopes are treated. For example, for the icosahedral cluster (Buckeyball⁸⁴) $C_{60}La$ (I rotational subgroup symmetry, 2 isotopes per atom,), the number of isotopomeric subunits for C, and La are

$$\begin{aligned} C & \quad (1/60)[2^{60} + (12)2^{12} + (12)2^{12} + (20)2^{20} + (15)2^{30}] \\ & \quad = 19,215,358,678,900,736 \end{aligned}$$

$$La \quad (1/60)[2^1 + (12)2^1 + (12)2^1 + (20)2^1 + (15)2^1] = 2$$

Hence we have 38,430,717,357,801,472 possible isotopomers of $C_{60}La$.

CHAPTER 8 CONCLUDING REMARKS

MCD and MLD have been shown to be very useful techniques for studying matrix isolated atoms and molecules. It has been shown that the SO constant of the lowest ^2P excited state of the noble and alkali metal atoms decreases in the order $Ar > Kr > Xe$, and that a supermolecule model nicely accounts for this trend. While attention has focused on the excited state, it would be interesting to analyse the matrix shift of the (average) $^2S \rightarrow ^2P$ transition energies for various rare gas hosts. This shift is the result of a differential matrix effect on the ground and excited electronic states. For the cases where experimental data exists ($Cu^{29,30}$, Ag^{85} and Au^{86}), it appears that the matrix shift is greatest in Ar and progressively decreases for the heavier noble gases. See Table 23. Possibly semiempirical calculations (EHT, CNDO, INDO, etc.), higher level ab initio computations, or even a phenomenological (Lennard-Jones, for example) approach applied to the MX_{12} entity would help to shed light on the mechanism of this matrix perturbation.

In addition, the moment analysis procedure which is so useful in studying atomic $S \rightarrow P$ transitions could probably be extended to encompass all transitions $^{2S+1}L \rightarrow ^{2S+1}L'$.

Table 22

Matrix Induced $^2S \rightarrow ^2P$ Transition Energy Shifts

System	Energy(cm^{-1})	Shift(cm^{-1})
Cu(gas)	30701	-
Cu/Ar	32763	2062
Cu/Kr	31911	1210
Cu/Xe	31712	1011
Ag(gas)	30166	-
Ag/Ar	32694	2528
Ag/Kr	31788	1622
Ag/Xe	30509	343
Au(gas)	39902	-
Au/Ar	42390	2488
Au/Kr	41231	1329
Au/Xe	39445	-457

This would enable one to extract ground and excited state information (SO constants, g factors, and Jahn-Teller couplings) from observed MCD and absorption spectra. Ideally, such a generalized equation should reduce to the simpler form upon allowing the replacements $L \rightarrow 0$ and $L' \rightarrow 1$ (ie. $S \rightarrow P$). Such a set of equations would undoubtedly be of great use in analysing the bulk of atomic spectroscopic transitions.

Application of the MCD saturation technique to Re atoms matrix isolated in Kr has revealed a large ground state SO mediated crystal field splitting which precludes the observation of any low temperature ESR. Sufficient thermal energy of the order 20cm^{-1} (30 K) is predicted to populate the $|U'\mu\rangle$ state resulting in the observable spin transition $|U'\mu\rangle \rightarrow |U'\lambda\rangle$. It would also be interesting to study via MCD the cases of Re matrix isolated in Ar and Xe to assess their ground state matrix splitting.

Faraday parameter expressions were derived that predict the MCD and MLD signs expected for the various electric dipole allowed transitions for randomly oriented linear molecules. While the MCD predictions are born out in the case of matrix isolated TaO⁸⁷ ($^2\Delta_{3/2}$ ground state), further experimental work needs to be done on other suitable linear molecules such as IO ($^2\pi_{3/2}$ ground state), CoO ($^4\Delta_{7/2}$ ground state), and IrC ($^2\Delta_{5/2}$ ground state) to test the theory. Also, it seems that one should be able to extend this treatment to the general molecular symmetry case and construct a table for each point

group that contains the expected low temperature MCD and MLD signs of all electric dipole allowed transitions. Maybe a simple prescription analogous to the atomic ΔJ selection rule exists that might enable one to say, for example, that all $T \rightarrow A$ molecular transitions are expected to be positive (regardless of any 1, 2, g, or u subscripts), etc.

APPENDIX A SIX COORDINATE SPIN-ORBIT REDUCTION FACTOR

In this section the expression for the SO reduction factor is derived for the case of a metal octahedrally surrounded by six rare gas atoms. The t_{1u} group orbitals composed of the rare gas $(n + 1)p$ atomic orbitals overlap with the metal p_x , p_y , and p_z orbitals.⁴⁴ The relevant molecular orbitals are

$$\phi_{t1u}(z) = c_1 p_z^M - c_2(z_1 + z_6) + c_3(z_2 + z_3 + z_4 + z_5)$$

$$\phi_{t1u}(y) = c_1 p_y^M - c_2(y_3 + y_5) + c_3(y_1 + y_2 + y_4 + y_6) \quad (163)$$

$$\phi_{t1u}(x) = c_1 p_x^M - c_2(x_2 + x_4) + c_3(x_1 + x_3 + x_5 + x_6)$$

When the SO Hamiltonian given in (6) is used to form the SO matrix, the result is similar to (7) except that the constant is different. Here it is called B and is given by

$$B = h^2(c_1^2 \zeta_M^2 - 2S_o \zeta_X c_1 c_3 + 2S_\pi \zeta_X c_1 c_3 - 2S_\pi \zeta_X c_1 c_2 + 2c_1 c_2 S_o \zeta_M + 4c_1 c_3 S_\pi \zeta_M)/8\pi^2 \quad (164)$$

The roots of the SO matrix are B (4 fold degenerate) and -2B (2 fold degenerate). The splitting (3B) is related to the effective SO coupling constant as done previously.

$$\Delta E = 3B \equiv 3\zeta_{\text{eff}}\hbar^2/8\pi^2 \quad (165)$$

The spin-orbit reduction factor is therefore

$$\begin{aligned} k \equiv \zeta_{\text{eff}}/\zeta_M = c_1^2 &- 2S_\sigma c_1 c_3 Q + 2S_\pi c_1 c_3 Q \\ &- 2S_\pi c_1 c_2 Q + 2c_1 c_2 S_\sigma + 4c_1 c_3 S_\pi \end{aligned} \quad (166)$$

where $Q \equiv \zeta_X/\zeta_M$. If the approximation is again made that the mixing coefficients are proportional to the appropriate overlaps (i.e., $c_2 \propto S_\sigma$ and $c_3 \propto S_\pi$), the coefficients can be expressed in terms of only one coefficient. Thus if c_3 is set equal to c, then c_2 becomes Rc where $R \equiv S_\sigma/S_\pi$. Again c_1 is taken ≈ 1 . Finally the reduction factor is

$$k = 1 + 2cS_\pi(2R - 1)[(R^2 + 2)/(2R - 1) - Q] \quad (167)$$

which is identical to the expression for the octahedral MX_{12} site model except that the numerical coefficient at the beginning of the second term is 2 instead of 4.

APPENDIX B S STATE CRYSTAL FIELD SPLITTING

In cases where the ground state multiplet originates from a Russell-Saunders's state of zero orbital angular momentum, there can be no crystal field splitting to first order. This arises from the fact that the crystalline electric field is spin independent and hence cannot split a state possessing only spin angular momentum. If the spherically symmetric S state can mix with a low lying P state via the spin-orbit Hamiltonian (selection rules: $\Delta J = 0$, $\Delta L = \Delta S = 0$, $\neq 1$), then one may observe a matrix splitting. In effect the mixing results in a distortion from spherical symmetry which renders the state susceptible to site symmetry perturbations. In such a situation, Eq.(45) is replaced by

$$|A\alpha\rangle = \sum_M \sum_{J'M}^A c_{J'M} [\sum_k d_k |J'M, k\rangle] \quad (168)$$

where the sum over k represents the mixture of excited states into the spherically symmetric (to first order) ground state.

Proceeding as before, we find that Eqs.(63)-(65) and (78) hold with the following replacements.

$$E_{CF_i} \rightarrow \sum_M \sum_{M'K} \sum_{A\alpha} C_{J'M'}^{A\alpha} C_{J'M'}^{A\alpha} d_k^2 \langle J'M, k | H_{CF} | J'M', k \rangle \quad (169)$$

$$\begin{aligned} \langle M \rangle^{(i,j)}_x &\rightarrow \langle M \rangle^{(i,j)} (\mu_B/kT) \sum_k d_k^2 g_k \\ &= \langle M \rangle^{(i,j)} g \mu_B/kT = \langle M \rangle^{(i,j)}_x \quad (170) \\ &= E_{Z(i,j)}/kT \end{aligned}$$

$$|\langle J' || m || J_f \rangle|^2 \rightarrow \left| \sum_k d_k \langle J', k || m || J_f \rangle \right|^2 \quad (171)$$

where $J_f = J' + 1$, J' , or $J' - 1$.

APPENDIX C
ZERO FIELD SPLITTING OF AN ORBITALLY NONDEGENERATE
MOLECULAR STATE

The MCD/MLD saturation formalism developed above for crystal field split ground atomic multiplets can be used with very little modification to treat the zero field splitting (crystal field and/or spin-spin and/or spin-orbit) of a molecular state $^{2S+1}\Gamma$ where Γ represents the totally symmetric representation of the appropriate molecular point group. In such a case (zero orbital angular momentum), one can use to lowest order an $|S M_S\rangle$ basis set to represent the ground molecular eigenstates⁷². The crystal field Hamiltonian, H_{CF} , is replaced by the zero field Hamiltonian⁴⁸, H_D

$$H_D = \sum_m \sum_n B_n^m O_n^m \quad (172)$$

where O_n^m are spin tensors of rank n ($n = 2, 4, 6, \dots$; $m < n$) and B_n^m are the expansion coefficients. In general, the spin tensors are zero for $n > 2S$, and the expansion coefficients decrease rapidly with increasing n .

If only the lowest order term is retained, we find for linear molecules ($m = 0$)

$$H_D = D[S_z^2 - S(S+1)/3] \quad (173)$$

In addition, the Zeeman energies are now given by $E_z = g\mu_B M_S$. Therefore we find

$$\Delta A_{MCD} \propto \pm (1/Z) \sum_{M_S > 0} \exp(-D[M_S^2 - S(S+1)/3]/kT) M_S \sinh(M_S x) \quad (174)$$

$$\Delta A_{MLD} \propto \pm (1/Z) \left\{ \sum_{M_S > 0} \exp(-D[M_S^2 - S(S+1)/3]/kT) x \right. \\ \left. \{ \cosh(M_S x) [3M_S^2 - J'(J'+1)] \} \right. \\ \left. - \exp(DS(S+1)/3kT) J'(J'+1)/2 \right\} \quad (175)$$

Note that the last term in the MLD expression applies only to the case of integral spin as it arises from the $M_S = 0$ spin component.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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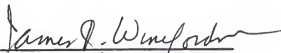
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